REMOVAL OF IMPURITIES FROM ELECTROLYTE SOLUTION TO PRODUCE PURE METALS

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BY

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ST. JOHN'S, NEWFOUNDLAND, CANADA.

.....To my beloved parents

REMOVAL OF IMPURITIES FROM ELECTROLYTE SOLUTION TO PRODUCE PURE METALS

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Abstract

The impurities present in the electrolyte solution not only deteriorate the quality of the metal product, but also may have large impact on the overall process efficiency. Therefore, solution purification before electrowinning process is an essential step for the metal to be electrowon. In this study, cobalt electrolyte solution was purified to produce pure cobalt and to improve process efficiency. A solvent extraction (SX) method has been examined to remove impurities such as manganese (Mn) and cadmium (Cd) from a cobalt electrolyte solution in a laboratory scale batch wise test work using modified D2EHPA (Di-2-ethylexhyl phosphoric acid). The organic reagent D2EHPA is an organophosphorous acidic extractant, which has an affinity to extract and remove metals from the electrolyte solution. The real cobalt electrolyte solution collected from Vale Inco's demo plant at Argentia has been used in this experiment.

By the SX method, metals were selectively removed from the cobalt electrolyte solution using modified D2EHPA, after converting its functional group with Na^{+} or Co^{2+} ions. The distribution ratio and separation factors were the key measures, in this experiment, to selectively remove the impurity metals from the cobalt electrolyte solution, and the separation of metals was greatly dominated by the equilibrium pH of the solution. It was found that D2EHPA modified by Co^{2+} was more favorable for controlling the pH of the solution. The concentration of organic extractant and the equilibrium pH of the solution were the important parameters to selectively remove the impurities from the cobalt electrolyte solution. A kinetic study was carried out showing the equilibrium position (rate of transfer of metals) between two phases. The stripping of metals from the loaded organic extractant was conducted using different concentrations of sulphuric acid

(H_2SO_4). Finally, a fixed concentration of H_2SO_4 was used for the stripping of the metals of interest. Mn and Cd were stripped with same concentration of H_2SO_4 which was the added benefit for the process. The kinetics for the extraction of Mn and Cd observed in the study were also found to be similar.

The screening tests with different ion exchange resins were also investigated in this study, to selectively remove manganese and other impurities. It was found that, among others, Amberjet 4400 CL followed by Amberlite IRC 748I and Lewatit TP–207 are suitable resins for the extraction of manganese and cadmium from a cobalt electrolyte solution.

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My special acknowledgement to my wife and two children, Tanzim and Tahmid, who sacrificed and deprived themselves from my companionship and recreation for the successful completion of my program.

I remember my late father who passed away during my program with great respect. I have had the ever great honor to acknowledge my father's affection and appreciation since my childhood until his death.

I also acknowledge my mother's appreciation with great honor. She has been giving me heavenly affection and advice to take care of my health and mental wellness over phone.

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List of Abbreviation and Symbols

Abbreviations:

Ag - Silver

Al - Aluminium

A/O or O/A – Aqueous/Organic or Organic/Aqueous, referring to volume ratio of the phases in contact

"aq" - Aqueous

Ca - Calcium

Cd - Cadmium

Co - Cobalt

D2EHPA - Di-2-ethyl-hexyl phosphoric acid

D.F. – Dilution Factor

EW – Electrowinning

HPAL – High Pressure Acid Leaching

IX – Ion Exchange

ICPMS – Inductively coupled plasma mass spectrometry

M – Molarity

Mg - Magnesium

Mn – Manganese

ND – Not Detected

"org" – Organic

PAL - Pressure Acid Leaching

PLS – Pregnant Leach Solution

POL – Pressure Oxidative Leaching

SX – Solvent Extraction

S.F. – Separation Factor

TBP - Tri-butyl-phosphate

VBN – Voisey's Bay Nickel

Symbols:

β – Separation factor

D – Distribution co-efficient

CHAPTER 1

Literature Review and Introduction

1.1 Background

Cobalt is a non-ferrous metal, which is not found as a free metal in the nature. Cobalt is generally found in the form of ores. It is not obtained as the principal product from the processing of any mine (Flett and Anthony, 1998), rather it comes as a by product of nickel and copper mining activities. Lateritic or oxide ore/concentrates are used to make a leach solution containing metals, such as nickel, copper, cobalt, manganese, magnesium etc. The leach solution is made by dissolving the ores/concentrates (e.g. nickel-copper laterite ores) in acidic solution. Trace amounts of other undesired metals are also dissolved in the solution, which are called impurities. If not removed, these impurities from the leach solution will be carried over to the electrolyte solution, and affect the performance of the electrowinning process, as well as deteriorating the quality of the metal product. Laterite ore is increasingly dominating the present market resources of nickel and cobalt. Moskalyk and Alfantazi (2002) highlighted the significant trend of laterite ore in the future, covering 70% of the resources of nickel in the world through pressure acid leaching (PAL) and solvent extraction and electrowinning (SX-EW) facilities, where cobalt is present as the associated metal. Mihaylov (2000) also mentioned that nickeliferous laterite ores would have a significant influence among the ore resources of nickel and cobalt in future. The author remarked that due to the

limitation of the ore upgrading process, the leach solution contains significant quantities of magnesium and manganese. It is important to know that the leaching conditions of ores have significant effects on the amount of impurities in the electrolyte solution. Briceno and Osseo-Asare (1995) investigated temperature effects on leaching and reported that with the increase of leaching temperature, the amount of impurities also increased, along with the increase of the concentration of desired metals. The concentration of cobalt is also significant among different metals in the industrial effluents and that is why cobalt electrowinning is proposed as the first step for treating the industrial effluents (Huang et al., 2004).

The use of cobalt is diversified and critical: cobalt-60 radiation source, superalloys for jet engines and in rechargeable batteries. Based on the statistical data from a study (Geovic Mining Corp, 2009) on global cobalt use for the year 2008, it was found that about 27% of cobalt is used in batteries, cell phones, computers, hybrid vehicles and portable tools, followed by 19% use in superalloys (turbine blades, mainly jet engines) and 18% in wear resistant alloys. In chemical industries, about 16% cobalt is used for producing pigments and dyes. Cobalt is also used as catalysts (9%) and magnets (7%). The use of cobalt, and its benefit, is significant to many industrial and commercial applications and that is why, the consumption of cobalt has been considerably increased in many countries. Geovic Mining Corp (2009) also reported on cobalt consumption by different countries and the increase for the four-year period ending in 2006, where it was found that percentile increase of cobalt consumption in China for the said period was 156 %, followed by Japan with 70%. In Europe and the USA the increase of cobalt consumption was the same (24%). From the above information, the necessity of cobalt can be clearly realized,

especially in China and Japan where the increase in the consumption of cobalt is more significant. In respect to the consumption, the production of cobalt is not yet up to the demand. That is why, the trend of price of cobalt is increasing and hence, there is increasing interest at the industry level to produce/recover cobalt from primary as well as secondary sources. Rane et al. (2005) remarked that the present sources of cobalt are not sufficient to meet the demand of the market and that is why secondary sources for recovery of cobalt are being increasingly exploited. However, enough publications regarding the technology involved in the cobalt recovery are not available (Sharma et al., 2005). The production of pure cobalt is also a major concern regarding consumption rate of cobalt. Xie et al. (2006) emphasized the determination of a trace amount of impurities in high purity cobalt to eliminate the adverse effects in the final cobalt product. Although cobalt is not designated as a major metal in the marketplace, it has a wide range of special applications where purity is a major concern. Elsherief (2003) reported that due to the presence of foreign cations in the electrolyte solution, current efficiency is adversely affected in the electrowinning process. In addition, this promoted the cracking and peeling of the desired metal. The author also studied the effect of temperature on cobalt electrowinning, and remarked that increasing the temperature to 50°C might benefit cobalt deposition, but hydrogen gas will be generated and its evolution will affect the current efficiency.

The source of the impurities in the cobalt electrolyte solution is the feed solution, which is typically called the "leach solution", or pregnant leach solution (PLS) in the metal extraction steps. As mentioned earlier, the leach solution is prepared by dissolving the ore/concentrate in an acid solution and this is done by a PAL or HPAL (High pressure

Acid Leaching) process. The solution enters into the solvent extraction process, consisting of extraction and stripping stages. The metal impurities along with the desired metals are also accompanied in these steps, unless they are removed. Sometimes, organic impurities are also entrained in the metal electrolyte solutions that are introduced through the intermediate SX route. Sole et al. (2007) carried out study on the removal of the entrained organic phase from zinc electrolyte, and reported that zinc electrowinning is very susceptible when organic impurities are present and, hence, it was emphasized in that study to ensure that trace amount of organics have been removed to the level of < 1 ppm from the advanced electrolyte.

In the present study, the cobalt electrolyte solution was collected from Vale Inco's Demostration Plant at Argentia. After analysis it was found that a significant quantity of manganese (Mn) was present as one of the impurities among others in the cobalt electrolyte solution. The cadmium (Cd) was another impurity in the cobalt electrolyte solution that was also removed in the present study using SX and IX methods. The advantages and disadvantages of small/excess amount of Mn in the cobalt electrolyte solution have been discussed in Chapter–2.

The separation of cobalt - manganese has not been reported enough in literature (Ocana and Alguacil, 1998). From the background study, it was found that the removal of manganese from cobalt electrolyte solution was usually carried out by oxidative precipitation, followed by liquid/solid separation to obtain a purified cobalt electrolyte solution, as it can be seen from a schematic of the original process employed in "Knightsbridge Cobalt of South Africa", where the feed material was oxide ore, which

was leached by sulphuric acid (Cole, 2002). It was found from the same study that calcium carbonate ($CaCO_3$) was used to get a precipitation of $CoCO_3$, which was purified after the precipitation of iron and copper. However, a sufficient purity of cobalt carbonate was still not achieved, as Cole (2002) remarked that higher prices could be realized if manganese and magnesium impurities were not present there. Different precipitation methods have been investigated and compared for the removal and recovery of manganese from a typical synthetic laterite waste solution by Zhang et al. (2009). The authors reported that hydroxide precipitation was not found efficient due to the poor selectivity for manganese, and a higher pH was also required. Regarding carbon precipitation methods, the author observed that substantial co-precipitation of magnesium was there in the process and manganese removal was not reached up to the requirement. Sulphide precipitation involved high operating and capital cost, as well as high temperature and pressure during operation, as reported by the same author. When the Mn content in the cobalt electrolyte solution is low, oxidative precipitation followed by solid/liquid separation is suitable (Babjak et al., 2006). In another study, Cheng (2002) mentioned three nickel laterite projects that have been commissioned in Western Australia, and the difficulties were found in every project using precipitation method. A similar high pressure acid leaching (HPAL) process was used for these three projects but the different drawbacks were found in the down stream processes including the process complexity, solvent degradation, crud formation as well as the capital cost that made the projects less appealing. In some cases, additional separation processes were followed to remove some other associated impurities. Legault-Sequin et al. (2004) studied the separation of Ni and Co from the impurities, such as Mn, Mg and Ca in the sulphate

laterite leach solutions, where the advantage of solvent extraction over precipitation method was emphasized and mentioned as the cost effective choice with simpler steps in the flowsheets. The precipitation method did not bring a desired solution to selectively and sufficiently separate manganese from cobalt in the electrolyte solution, and investigations on various methods were dismissed for the selective removal of manganese from the leach liquor by oxidation to Mn^{4+} (Cole, 2002). That is why, in the present study, solvent extraction and ion exchange methods have been considered in the purification of a cobalt electrolyte solution to produce pure cobalt.

1.2 Introduction to Extractive Metallurgy and Solvent Extraction (SX)

Extractive metallurgy deals with the processes involved in mineral processing for the production of a desired metal. Metal extraction processes were developed to recover and produce high purity metals from mineral compounds. Most metals are found in nature as compounds, such as mixtures of sulfides, oxides, carbonates and silicates. Usually, mineral found in nature require a great deal of pre-treatment prior to the extraction steps, such as pyrometallurgical or hydrometallurgical treatment. Pyrometallurgy involves operations where furnace treatments at high temperatures are used to convert and refine the ores in order to separate the metal through roasting, smelting, converting and refining. On the other hand, hydrometallurgy involves aqueous and organic solutions for the extraction of metals from ores/concentrates or secondary sources. Leaching, solvent

extraction, and electrowinning are the common processes in hydrometallurgy. There are a variety of treatment options for metal recovery that utilize physical, chemical and electrochemical techniques, such as chemical precipitation, solvent extraction (SX), ion exchange (IX), oxidation precipitation and electrowinning (EW). A generalized metal recovery flowsheet, incorporating solvent extraction, is shown in Figure 1.1.

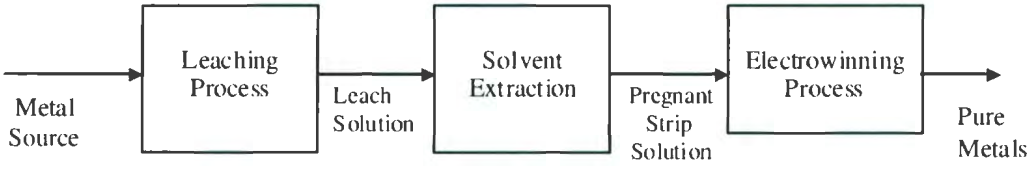


Figure 1.1 Generalized metal recovery flow diagram for solvent extraction

Hydrometallurgy has an environmental advantage over conventional smelting, where waste products in the process are generated as solids which can be easily contained instead of air emissions in the case of pyrometallurgy. Therefore, mining industries are presently adapting the hydrometallurgical process considerably. However, the environmental issues are being significantly considered at the industry level, and that is why efficient, cost-effective and sustainable hydrometallurgical processes are to be adopted.

In the solvent extraction method, selective separation and extraction of valuable metals from an aqueous solution are achieved through the introduction of an organic solution. In this procedure, the aqueous solution containing the desired metal is mixed (extraction)

with an organic solvent containing a reagent which extracts the metal ions. When metal species transfer from an aqueous solution to an organic solution, it is obvious that there must be some chemical interaction which causes this to happen and it is the extractant (also called reagent) in the organic solution that interacts with the metal. The roles of extractants have been discussed in a latter section. After the emulsification of aqueous and organic phase the selected metal (the metal of interest) reacts with the reagent to form a chemical compound and is transferred to the organic solution. The metal loaded organic phase is then separated from the aqueous feed solution and stripped with an aqueous solution and made ready for eletrowinning. The organic solution is recycled back to the SX circuit for further extraction, either directly or after a fraction of it has been cleaned for impurities. The whole process is shown in Figure 1.2, where cathode metal was produced from the ore/concentrate using leaching and SX-EW process.

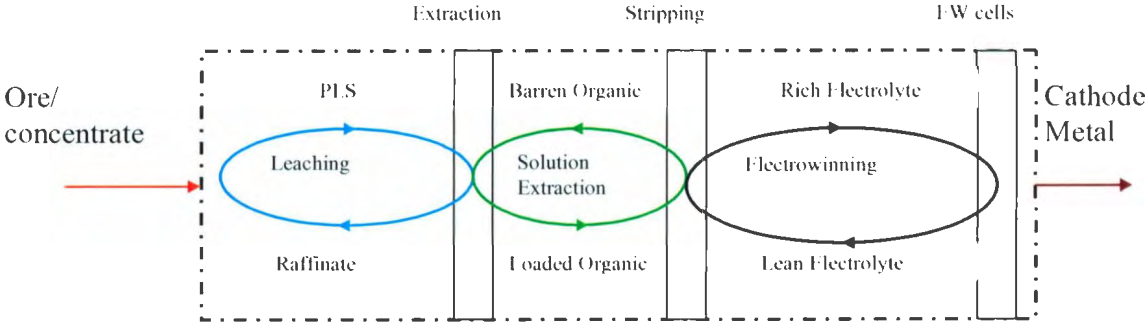


Figure 1.2 Solvent extraction-electrowinning process

A simple solvent extraction process is shown in Figure 1.3, where impurity metals were removed from cobalt electrolyte solution.

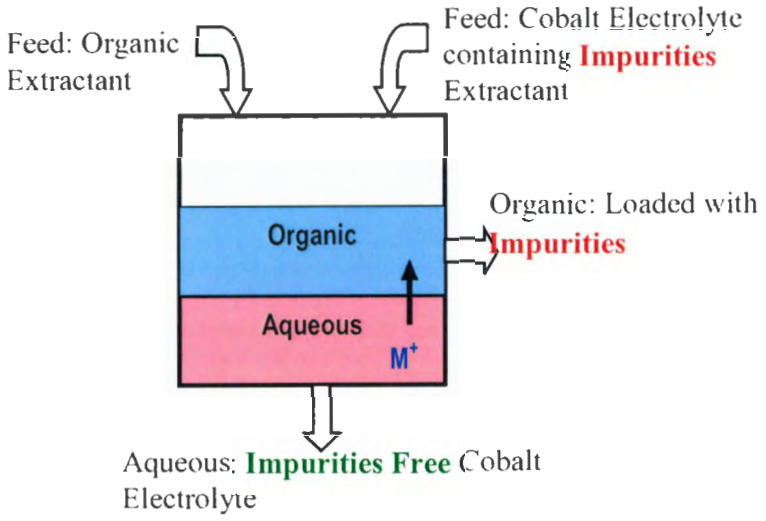


Figure 1.3 Simple solvent extraction process

As can be seen from the figure (Figure 1.3), the impurity metal ion is being transferred to the organic phase during emulsification and separation stage.

Figure 1.4 shows the separatory funnels which are used to separate organic and aqueous from their mixtures after the solvent extraction test. The aqueous raffinate solution is collected from the bottom layer, leaving the organic layer at the top. In the interest of producing the best phase separation i.e. to remove the trace amount of organic substances from the aqueous solution during separation process, phase separating paper as well as the centrifuge machine (Eppendorf 5810: at 2000 rpm and 5 minutes) was used in this study.

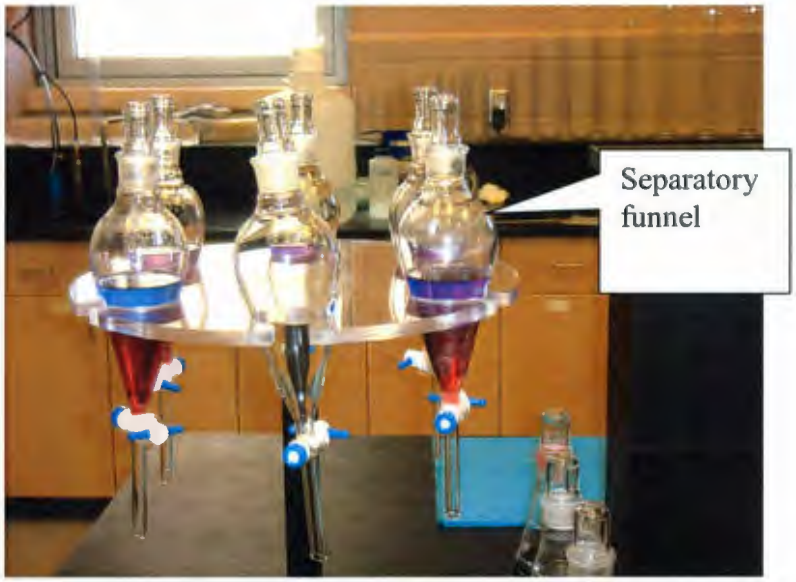


Figure 1.4 Phase separation in solvent extraction process

Earlier, solvent extraction was applied to higher value metals with limited operation, but through the invention of new reagents and improved process control and equipments, solvent extraction circuits and operations have also been improved (Littlejohn et al., 2007). The technology in the solvent extraction process is now applicable for the lower value metals due to the availability of new extractants, with improved selectivity, and other favorable criteria. Cheng et al. (2004) carried out a study for the separation of manganese from the nickel laterite leach solution (waste), using synergistic organic system, and reported that a significant extraction of manganese was attained. Sadanandam et al. (2008) carried out a pilot plant study to produce a high purity cobalt oxalate from the leach solution of the spent ammonia cracker catalyst, where a mixed extractants system consisting of D2EHPA (Di-2-ethylexhyle phosphoric acid) and TBP (tri-butyl- phosphate) were used in the solvent extraction process to remove major impurities, such as iron and aluminium .

Solvent extraction is a common and efficient method of recovering metal ions from a leach liquor or to remove impurities from an electrolyte solution, and it causes less process burden if compared to the precipitation method. This process has been in use for long time in the mining industry for purification of metals. Solvent extraction process was so far successfully demonstrated to be one of the most economical methods for metal recovery. In separation processes of hydrometallurgy, solvent extraction has become crucial where the phosphorous-based extractants have special importance (Flett, 2005). Solvent extraction method is suitable for extraction of metal, however precipitation method is also accompanied or followed by SX method for complete removal of impurities from the whole process. Solvent extraction involves low energy consumption, small volume of waste disposal and absence of toxic component (Hoh et al., 1984). Louis (2009) investigated the SX and precipitation methods for the cobalt solution purification. Regarding the SX method, the author remarked in the conclusions that using D2EHPA with the optimized SX route, losses of cobalt can be minimized to 0.5 % or less. The purification through the solvent extraction route would be feasible when the concentrations of impurities are much lower than the desired metal concentrations. Otherwise, the process may lead to a higher flow rates in the SX routes requiring larger volume of associated equipment.

In the present market, many kinds of organophosphorus acid, such as di-(2-ethylhexyl) phosphoric acid (D2EHPA), 2- ethylhexyl phosphoric acid mono-2-ethylhexyl ester (PC 88A), bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) etc. are available, which can be used to make the separation process feasible. It is important to find out the selectivity of an extractant for the extraction of a particular metal from a leach or an

electrolyte solution. Selectivity, as well as proper concentration of an extractant is important for the extraction of desired metals. That is why, Devi et al. (2000) remarked that the use of solvent extraction in the separation of manganese, cobalt, nickel and zinc from sulphate solutions is tricky. Owusu (1998) carried out a bench scale solvent extraction study using 30 vol. % D2EHPA in an mixed electrolyte solution, that contained sulphates of Zn, Cd and Co, and reported that cadmium was extracted at pH 3.7. Vahidi et al. (2009) used D2EHPA in kerosene for the recovery of zinc from an industrial zinc leach residue, and all zinc were extracted from the aqueous solution at pH 2.5, with 20% (w/w) D2EHPA. An organophosphorous acid, such as D2EHPA has the ability to extract cationic species from an aqueous solution, where hydrogen ion in the extractant is replaced with the metal ion. Extraction pH, operating temperature and other factors, such as aqueous concentration, metal-extractant complex, A/O ratio also have significant role in the extraction, along with the type of the extractant and its concentration. Preston, J.S. (1982) reported that cobalt is extracted at lower pH than nickel and from the comparative study of different acid groups, it was found in the study that cobalt – nickel separation increased in the order of phosphoric < phosphonic < phosphinic acids. In comparison to the extraction pH value it was found that Cyanex 272 needs higher pH values than D2EHPA to extract the same metal ions (Silva et al., 2005). This happens, as phosphinic acid derivatives are weaker than the derivatives of phosphoric acids.

1.3 Literature Review on Extraction of Manganese by SX Method

Manganese is associated with copper and nickel minerals, and carried over to the stream of cobalt electrolyte through the leach solution, which over time can build up in processing circuits. Manganese has an adverse effect in the SX routes as well as in the EW circuits and that is why, it is important to remove from the solutions. Babjak et al. (2006) mentioned that the lateritic or oxide ores are the sources of cobalt, which also contain different elements including Mn, which is difficult to separate due to its similarity in chemical properties with that of cobalt. Manganese impurity in the electrolyte solution affects the electrowinning process of other metals, such as copper and zinc. Zhang and Cheng (2007b) reported that the presence of manganese impurity results decrease in the current efficiency during copper electrowinning, and also degrades the solvent in SX steps, when oxidized to a higher valent manganese. In the beginning, the presence of manganese (II) does not affect much in the SX plant but over time manganese (II) in the electrolyte is oxidized to higher valence that leads to the reduction of conductivity of the electrolyte causing lower current efficiency of the plating operation during electrowinning process (Littlejohn, 2007). It is worth mentioning here that due to the oxidation reactions, organic reagent also oxidizes, that leads to the solvent degradation, phase separation difficulties and reduction in the plant performance. Electrowinning of cobalt is also affected by organic impurities. Mishra et al. (2002) studied on different organics that affect electrowinning of cobalt from the sulphate solutions. The authors reported that D2EHPA was found to have the highest current efficiency (90%), and lowest with Versatic 10 (2-hexylmethyl decanoic acid). Devi et al. (2000) carried out

study on the separation of the divalent manganese and cobalt from the sulphate solution using sodium salts of D2EHPA, PC 88A and Cyanex 272 in kerosene, and observed that extraction of metals increased with the increase of equilibrium pH, and it happened in the case of all extractants. It was reported that equilibrium pH of 4.45 was most suitable for the extraction of the manganese over cobalt at the separation factor 79.3. The separation of manganese from cobalt in the sulphate solution was studied by Hoh et al. (1984) using D2EHPA, where pH of the aqueous and organic phase was maintained at around 4.2 and 2.0, respectively. Ajgaonkar and Dhadke (1996) used Cyanex 302 in toluene to extract cobalt and manganese from the sulphate solution, where it was found that cobalt (II) was extracted at pH 7.0 – 7.5, and pH range for quantitative extraction of manganese was 8.5 – 9.5. It happened, as the Cyanex 302 is an organophosphinic acid unlike D2EHPA (organophosphoric acid). It is noteworthy that extraction of metals varies greatly with extraction pH. Cheng (2000) studied on the separation of manganese from cobalt using nickel laterite leach solution with D2EHPA. The author reported that the manganese separation was optimum at pH 3 at room temperature (23°C), and manganese concentration was reduced from 2 g/L to 3 mg/L by two theoretical stages obtained by McCabe–Thiele diagram at pH 3.5 and temp. 40°C. Zhang and Cheng (2007a) reviewed the separation and recovery of manganese from Co and Ni using D2EHPA. The authors reported that using D2EHPA, manganese was separated from cobalt at pH 4.2, when the operation was continuous. The optimum pH was 3 for the separation of Mn from Co at temp. 23°C. However, the separation of Mn from Co at optimum pH 3.5 was done at the temperature range 40-60°C. Co-extraction of cobalt and manganese occurs at higher pH in the extraction phase. Agatzini-Leonardou et al. (2009) carried out study on the

separation and recovery of nickel from sulphate heap leach liquor of nickeliferrous laterite ores using SX method. The authors reported that cobalt, manganese and magnesium were extracted using 20% Cyanex 272 at pH 5.5 and temp. 40°C. In the same study, cobalt and manganese over magnesium were extracted at pH 5.0 using Cyanex 302 with same concentration and operating temperature. Cheng and Urbani (2005) reported that lower temp (< 15°C) results high viscosity and higher temperature (> 60°C) may lead to the loss of organics by degradation and evaporation.

Legault-Sequin et al. (2004) used Cyanex extractants (272, 301 and 302) for the direct extraction of Ni and Co from the major impurities (Mn, Mg and Ca) associated with the laterite leaching, where the impurities were left into the solution instead of being extracted. It was reported that Cyanex 301 and Cyanex 302 were selective for cobalt. On the other hand, D2EHPA was selective for Mn extraction which was found from the literature search, as well as from the screening test of the present study. It is noteworthy that the same extractant is selective for different metals but at different conditions. For example, Zn also can be extracted by D2EHPA but at lower extraction pH compared to that of Mn. Panigrahi et al. (2009) studied processing of manganese nodule leach liquor, where Zn was separated with D2EHPA. The present study considered the effects of different factors, such as equilibrium pH, extraction time, and extractant concentration during the extraction process. The choice of equilibrium pH is crucial, as the extraction of Mn is pH dependent. Devi et al. (2000) investigated that for different extractant concentrations used in their study, the separation factor decreased with increasing equilibrium pH. The pH value in the case of different concentrations of PC 88A and Cyanex 272 was within the range of 2.77 – 7.50. In the case of D2EHPA, the selectivity

for manganese was higher than that of cobalt; i.e. manganese was extracted at lower pH compared to that of cobalt. The best separation factor in the present study was observed at pH 3.5 and this pH was found suitable for the selective separation of manganese over cobalt. Higher pH was not favorable because of co-extraction of cobalt, when P^H exceeds the above value, which is discussed in Chapter 2 and Chapter 3.

Tsakiridis and Agatzini (2004) studied on simultaneous extraction and separation of Co(II) and Ni(II) from manganese and magnesium sulphate solutions, where the interaction effects were also considered along with the main effects, such as extraction pH at equilibrium, temperature, extractant concentration and organic to aqueous phase ratio.

1.4 Literature Review on Extraction of Cadmium by SX Method

Cadmium (Cd) impurity can adversely affect on the quality as well as the profitability of the cobalt product. Cadmium removal from the electrolyte solution prior to electrowinning is necessary, otherwise the cadmium will be carried over to the EW cell that will contaminate the cathode plate of the desired metal. Mihaylov and Hope (2009) reported that the nickel solution produced by pressure oxidative leaching (POL) from Voisey's Bay Nickel (VBN) concentrates typically contains 2 – 4 mg/L cadmium which eventually may increase to 50 – 100 ppm in the final nickel product that may have significant negative effect on the marketability of that product. The authors also mentioned that though cementation method is used to remove Cd from leach solution in

the zinc refinery, however, this method is not applicable in the case of Co and Ni system, as Cd is less noble than cobalt and nickel, hence it may lead to a loss in Co/Ni production. It is always expected that, to produce any desired metal, the impurities will be removed or extracted as far as possible with minimum co-extraction of the desired metal. This explains why the selectivity of a suitable extractant for the removal of an impurity is important as previously mentioned. Different authors studied on the extraction of cadmium from a leach solution or from an electrolyte solution using organophosphorus acids. Kumar et al. (2009) studied solvent extraction process for the extraction of cadmium from a sulphate solution, using di-(2-ethylhexyl) phosphoric acid (D2EHPA) with 1% isodecanol in kerosene diluent. In that study, the extraction of cadmium was found feasible at an equilibrium pH of 4.5 with 1:1 O/A ratio in a single contact and the metals were effectively stripped from the loaded organic using 180 g/L (1.84 M) sulphuric acid. But it is worth mentioning here that in this study, the cadmium was extracted as the desired metal from the high tenor cadmium solution instead of being removed as the impurity. That is why, the equilibrium pH 4.5 was suitable to extract cadmium. However, when minor amount of cadmium needs to be removed selectively from another metal ion in the electrolyte solution, controlling of equilibrium pH is a major factor. Otherwise, the desired metal (cobalt in the present study) may be co-extracted with the impurity metal at the same pH level.

Almela and Elizalde (1995) used bis-(2,2,4-trimethylpentyl) thiophosphinic acid (Cyanex 302) in kerosene for the extraction of cadmium from the chloride media of ionic strength 1.0 M. However, it was found from another study (Mihaylov and Hope, 2009) that cadmium was removed by solvent extraction from nickel or cobalt sulphate solutions

using organophosphorus acidic extractants where the extraction results for cadmium was progressively reduced when the solutions contained increasing amounts of chloride. Reddy et al. (2004) reported the solvent extraction of cadmium from sulphate solutions using the commercial extractants: TOPS 99, PC 88A and Cyanex 272 and their mixtures. The study showed the dependence of the cadmium extraction on equilibrium pH of the aqueous phase and extractant concentration. Other parameters were also considered, such as metal concentration, synergism, different kind of salts and loading capacity, which have significance on that study. Safarzadeh et al. (2007) reviewed several studies on the hydrometallurgical extraction and recovery of cadmium from various resources, and remarked in general that organophosphoric acid D2EHPA is the most useful extractant for the extraction of zinc and cadmium from complex solutions. Afsari et al. (2009) investigated solvent extraction of cadmium (II) from the stock solution of cadmium (II) sulphate by bis (2-ethylhexyl) phosphoric acid (D2EHPA) diluted in toluene. Optimum pH range for the extraction of Cd (II) was 5 to 6. Loaded cadmium was stripped with a high concentration (4.0 M) hydrochloric acid. Noqueira et al. (2009) carried out study on the separation of cadmium, cobalt and nickel from sulphate solutions by solvent extraction using the nickel loaded extractants, where it was reported that the cadmium was extracted at pH 3.8-4.3 while cobalt was extracted at pH 5.1-5.7.

In the present study, removal of cadmium was studied through solvent extraction process with an organophosphorus acid (D2EHPA) in 1-decanol and Escaid 110. A significant amount of cadmium was extracted by using 25 vol. % Co-D2EHPA at around pH 3.5, which has been discussed in Chapter – 3.

1.5 Introduction to Extractant, Diluent and Modifier

Usually in solvent extraction process, the key topics such as chemistry and kinetics of solvent extraction as well as engineering theory of liquid-liquid extraction and phase separation phenomena are involved. The components of organic solution that play an important role in solvent extraction are: (1) Extractant (2) Diluent (3) Accelerator, and (4) Modifier. A brief introduction of each of them are as follows:

Extractant: The extractant is an organic chemical reagent that forms an organic soluble complex (metal-extractant complex) after reacting with the metal ion in aqueous solution, where the organic soluble complex is preferentially distributed to the organic phase. Mihaylov (2009) mentioned that in solvent extraction (SX) - the organic is the convenient "shuttle bus" between two aqueous solutions. In solvent extraction step organic extractant is loaded with the target metal ions (impurity metals in this study), when mixed with the leach solution, and is unloaded in the stripping step when comes in contact with the strip solution. The loading and unloading process of the organic extractant is shown in Figure 1.5

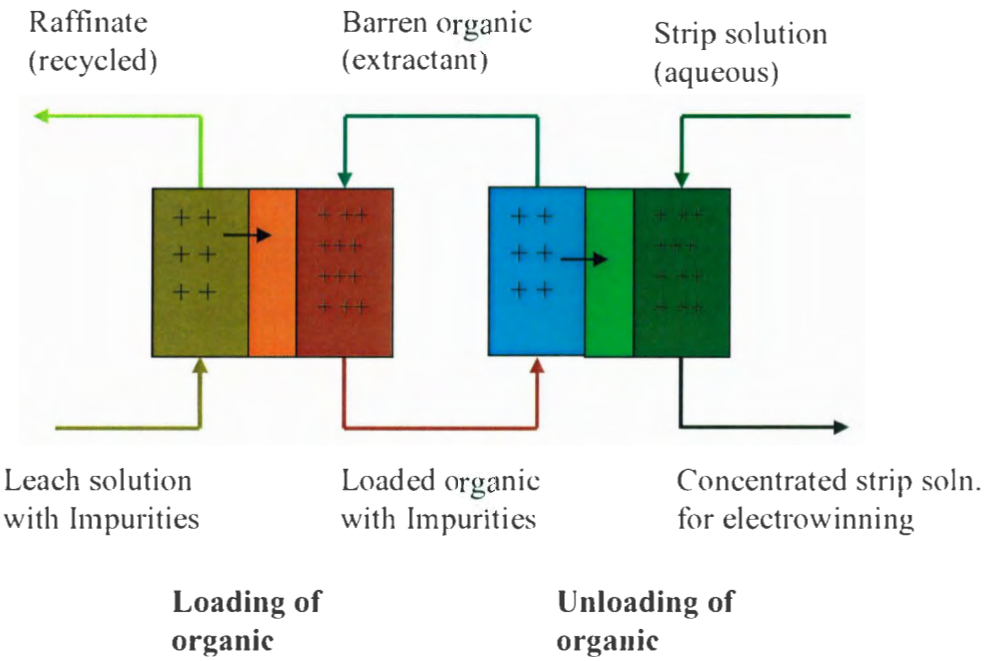


Figure 1.5 Loading and unloading cycle of an organic extractant in SX process

In solvent extraction process, an extractant should have a number of criteria for satisfactory performance in the recovery and purification of metals present in the aqueous solution. However, advantages and disadvantages exist when an extractant is selected for any particular application (Rotuska and Chmielewski 2008). Usually, an extractant (reagent) should have some basic requirements, such as good ability to extract the metal at the required pH, selectivity for the desired metal, rejection of impurity metals, good kinetics (rates of extraction, stripping) and stability. An extractant also should be cheap and available. A good balance of all the criteria is important, although all the advantages do not exist in a particular extractant. In this study, the extractants are the converted D2EHPA i.e. Na-D2EHPA and Co-D2EHPA.

Diluent: A diluent is an organic solvent that dissolves the extractant as well as metal-extractant complex and is used to dilute the extractant concentration to the appropriate level for metals extraction and stripping. The diluent provides the required physico-chemical properties of the SX system. It should be commercial and readily available. The diluent should not take part in the reaction during solvent extraction process. An aliphatic diluent has some good criteria, such as it provides better extraction, good separation factor, faster equilibrium and ease of phase separation, that is why, it is preferred over an aromatic diluent (Mohapatra et al., 2007). In this study, the diluent used in the experiment is Escaid 110, which is an aliphatic kerosene.

Modifier: A modifier is added to a solvent to improve its properties e.g. by increasing the solubility of an extractant and also improving the phase separation properties of the SX system. In this study, 1-decanol was used as the modifier.

1.6 Introduction and Literature Study on Ion Exchange Method

Ion-exchange technology is a modern approach in chemical analysis and has prospective applications in medicine, biochemistry, biotechnology and at pharmaceutical industries. Although in hydrometallurgy precipitation and in some cases precipitation followed by solvent extraction methods has been used, however, ion-exchange technology for the separation and purification of metals are being implemented in the metal industries considerably, where ion exchange resins/chelating agents are used as the exchangers for adsorption of metal ions. In the separation process, the selection of ion exchange material

is crucial which is affected by the scale of separation process, economical considerations, questions of environmental safety and regulations, and some others (Zagorodni, 2007). Ion exchange resins are included in the scope of the most important and scientific developments of the 20th century in the diversified field including the hydrometallurgy and environmental remediation (Alexandratos, 2009). The operation and control of ion exchange method is easier compared to the solvent extraction method.

Ion exchange may be carried out under equilibrium conditions, i.e. a certain volume of solution is contacted with a certain weight of resin and shaken long enough till equilibrium is reached. Under such conditions, the uptake of any species on a resin is characterized by the distribution co-efficient D, defined by

$$D = \frac{\text{Conc. of metal ion in resin phase}}{\text{Conc. of metal ion in aqueous phase}}$$

The higher the value of D, the higher is the affinity of the resin for that particular metal ion. Two types of ion-exchange resins: Amberlite® GT73 from 'Rohm & Haas' and Lanxess' Lewatit® TP 214 are known to be capable of selectively removing cadmium (Mihaylov, 2009).

Strong and Henry (1976) investigated the purification of cobalt advance electrolyte using chelating ion exchange resin TP 207 (Bayer's product) for the removal of trace amounts of copper and zinc when the solution pH was 5 – 6. The cobalt raffinate was received

from the copper solvent extraction plant and then a preliminary purification was carried out by lime precipitation, but still the impurities concentrations were high in the advance electrolyte. Eventually, they used the ion exchange method and remarked as the efficient technique to meet the desired copper specification 0.0001 g/L (0.1 ppm), which was very less than the maximum permissible levels of impurities (10 ppm) in Co metal. Zainol and Nicol (2009) used chelating ion exchange resin "Amberlite IRC 748", that contains iminodiacetate acid functional group, and investigated the adsorption properties of Ni, Co, Mn and Mg at different pH values. In that study, it was possible to separate manganese at pH 5 from cobalt due to the high selectivity of cobalt.

Ion exchange resins are spherical beads having a chemical structure based on crosslinked three-dimensional polymer molecules into which particular functional groups (such as sulfonic acid) are introduced. Based on the type of functional group ion exchange resins are classified as cationinc and anionic. A cation exchange resin exchange positive ions such as Ca^{2+}, Mg^{2+} and an anion exchange resin exchanges negative ions such as Cl^{-}, SO_4^{-2}. Based on the acidity and alkalinity, they are classified as strong or weak exchangers. There are special type resins named chelating resins having functional groups that form chelates with metal ions. Chelating resins have a higher selectivity for a particular metal ion.

In the separation and purification technology, ion exchangers are determined based on their affinity or selectivity for adsorption of particular metals interested for. Ion exchangers (cationic or anionic) are macroscopic, solid, high molecular polymer substances, insoluble in water with a functional group (exchangeable ion) which determines the properties (chemical or physical) of the resin. Ion exchangers based on

synthetic resins are mostly used as the modern ion exchangers. However, chelating resins are also used for determining the high selectivity of particular metals in the separation process. Koivula et al. (2004) carried out study on the removal of some metals from the effluents of metal-plating industry using chelating ion exchangers. The authors remarked that the precipitation technique is not an efficient method to meet the environmental regulations up to the desired level, instead, ion exchange would be an effective technique for the metallurgical industries to prevent the harmful effluents, as well as to reduce the waste.

Experimental conditions in the ion exchange method are very important and different factors are necessary to consider, such as pH, concentration of metals in the electrolyte, temperature, kinetics, type and condition of resins. Mendes and Martins (2004) reported that the sorption and desorption kinetics, as well as the selective loading characteristics of some chelating ion exchange resins are governed by both of the target metal and the competing metal concentrations. Gode and Pehlivan (2003) carried out a comparative study of two chelating ion-exchange resins (Lewatit TP 207 and Chelex-100) containing iminodiacetic acid groups for the removal of the chromium (Cr) from the aqueous solution and it was observed in the study that solution pH had a strong effect on the equilibrium constant of Cr(III). In the present study, the screening test was based on the pH of the original cobalt electrolyte solution at pH =2.95). Also the changes in temperature cause slight increases in the values of the equilibrium constant for the sorption, and significant changes of adsorption of metal ions as found by Gode and Pehlivan (2003).

1.7 Literature Study and Introduction to Stripping

The term stripping is also called as 'back-extraction' in SX process. In the case of ion exchange, the term is used as 'elution'. As of general procedure in liquid-liquid extraction, the loaded organic is mixed with a suitable strip solution (e.g. low concentrated acidic or alkaline solution) at a particular A/O ratio and the two phases are then separated when equilibrium is reached (Rydberg et al., 2004). Once the metal ions are extracted by the solvent extraction process, the next step with main difficulty is the recovery of metal ions loaded in the organic, and it depends on the metal ions-extractant complex in the solution (Zagorodni, 2007). In the present study, sulphuric acid (H_2SO_4) solutions with various concentrations were used as the stripping agent to strip metal ions from the loaded D2EHPA. Different authors also used sulphuric acid solution to separate metals from the loaded organic (Sandhibigraha et al., 2000; Gu et al., 2000; Ortiz and San Roman, 2002; Mohapatra et al., 2007; Huo et al., 2007; da Silva et al., 2008 and Arroyo et al., 2008).

Mohapatra et al. (2007) reported that complete stripping of aluminium (Al) from the loaded organic was possible using 1.0 M H_2SO_4 at an A/O ratio 1 and in a single stage. Arroyo et al. (2008) carried out study on silver (Ag) extraction from the acidic thiourea solutions using thiosubstituted organophosphorus acids as the selective extractants. It was reported in that study that complete stripping of Ag(I) from the loaded organic was ensured using a mixture of NH_4SCN (ammonium thiocyanate) and H_2SO_4. Gupta et al. (2004) extracted indium using Cyanex 923 by liquid-liquid extraction and the extracted metal ions were recovered by stripping with 1 M H_2SO_4. Senapati et al. (1994) carried out study on the purification of nickel sulphate solutions containing iron, copper, cobalt, zinc

and manganese through the solvent extraction and precipitation methods. Manganese was one of the impurities in the acidic nickel bearing solution which was stripped from the loaded organic with 0.5 vol. % H_2SO_4, and it was done in a single stage. Wang and Fthenakis (2005) conducted feasibility study on the recycling of cadmium-telluride photovoltaic modules which was leached using H_2SO_4-H_2O_2 (sulphuric acid-hydrogen per oxide) and the metal extraction was carried out by the cation exchange resins. It was reported in that study that elution of resins required high strength of H_2SO_4. Sze and Lam (1999) used the solvent extraction method for the treatment of spent electrolyte solutions generated in nickel-cadmium (Ni-Cd) rechargeable battery manufacturing industry. Ten extractants were tested in that study, and among them Kelex 100 was found to be an excellent extractant while 0.1 M H_2SO_4 or 0.1 M HCL solution was used as an stripping agent.

1.8 Metal Analysis/Data Measurement by ICP-MS and Statistical Summary

In this experiment, the metal concentration in the aqueous phase was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), model: Perkin Elmer ELAN DRC II. The metal concentration in the organic phase was obtained from the mass balance of metal concentrations in the feed and raffinate solutions. Brief procedures of data measurement by ICP-MS has been provided in Appendix E1. Based on the procedures, a sample calculation and results for the extraction concentrations of metals (Mn, Co and Cd) from kinetic study is provided in Appendix E2.1. The calculated data

(using MS Excel) were compared with the data measured by the ICP-MS (Appendix B6, Run # m32146m, Exp. Sample # CK-1). The observed errors for Mn, Co and Cd was -0.5%, 1.72% and 0.37%, respectively which are very close to the data measured by the ICP-MS using computer software. It might happen as the instrumental drift is calculated and corrected during measurement with the ICP-MS. Drift is monitored from internal standard elements Sc (Scandium), Rh (Rhodium), Re (Rhenium) and Th (Thorium). It was found from a study (Friel et al., 1990) that during analytical procedures by ICP-MS other factors such as, matrix effects, instrumental drift and molecular ion interference have also effects on the results.

Statistical estimates such as mean, standard deviation and RSD (relative standard deviation) were also done from the repeated measurements for finding the uncertainty of data measurements. Relative standard deviation (RSD) indicates the precision of data measurement i.e. it shows the reproducibility or repeatability of measurement and is calculated as follows:

RSD= (Standard Dev)* 100/Mean .....(1.0)

The RSD for the sensitivity measurement of kinetic study data from 6 repetitive standard measurements (Appendix E2) were calculated and presented in Appendix - E (E2.11, E2.12 & E2.13). The RSD for Mn, Co and Cd concentration was found to be 1.95 %, 9.94% and 3.16%, respectively. From the above statistical estimates it can be said that measurements for Mn and Cd concentrations will vary ± 1.95% and ± 3.16% of the data values if the measurements are repeated. In case of cobalt, the RSD is higher but it is still within the range of 10%. Another sample data of sensitivity measurement (cps) of the stripping study, from the three repetitive standard measurements (Appendix - E3) were

statistically analyzed and the RSD found for Mn, Co and Cd were 4%, 3.4% and 4.4%, respectively (Appendix E3.1, E3.2 & E3.3), which are also within the acceptable precision limit. The same results also can be found in Appendix E5 (received from the analysis performed by the ICP-MS).

1.9 Subject of Investigation

The subject of investigation for Mn and Cd separation from the cobalt electrolyte solution is divided into two methods as follows:

I. Solvent Extraction (SX) method using the extractant D2EHPA after converting its functional group.

II. Ion Exchange (IX) method using different resins.

In this study, only a screening test was conducted for IX method to find out the selective resins for the extraction of manganese and cadmium.

In SX method, the investigation comprised four distinct phases. The first one was the selection of extractant, diluent and modifier for use in SX process. The second phase included a study of the modification of D2EHPA by Na^+ and Co^{2+} ions to control the equilibrium pH. The third stage was the study of the effect of the equilibrium pH, extractant concentration and kinetics of extraction. The fourth one was the stripping of loaded organic with different concentrations of H_2SO_4. The results of four phases of this investigation are reported later in this thesis. Ion exchange method using different resins has been discussed in Chapter – 4.

1.10 Objective of the Study

The objective of this study was to remove impurities from a cobalt electrolyte solution by the SX/IX method with the target of achieving pure cobalt production as well as optimizing the process parameters. In the research field, there are many methods to remove impurities using different hydrometallurgical techniques, such as precipitation, cementation, solvent extraction and ion exchange. Among them, solvent extraction and ion-exchange processes are comparatively efficient and better from a practical point of view. In the present study, different solvent extractants and ion exchange resins were tested and investigated in screening tests to selectively remove impurities from the cobalt electrolyte solution.

The study might be useful to obtain preliminary design criteria for the development of a process flow sheet, or to include an additional impurities removal stage in the current hydromet process flow sheet of Vale Inco to treat cobalt electrolyte solution during pressure leaching of Voisey's Bay nickel sulphide concentrate. The proposed area for the purification stage of cobalt electrolyte solution is shown with a circle in Fig. 1.6, which is based on the flow sheet of Vale Inco's Hydromet Process published in their quarterly newsletter 'The Gossan', 2009.

This research will help in the optimization of separation processes for the recovery of pure cobalt, and it will create a greater profit of the concerned industries. The scope of work of this research includes:

- Reviewing of existing technologies/processes

- Investigation of the alternatives for the present technologies or processes
- Process parameters optimization

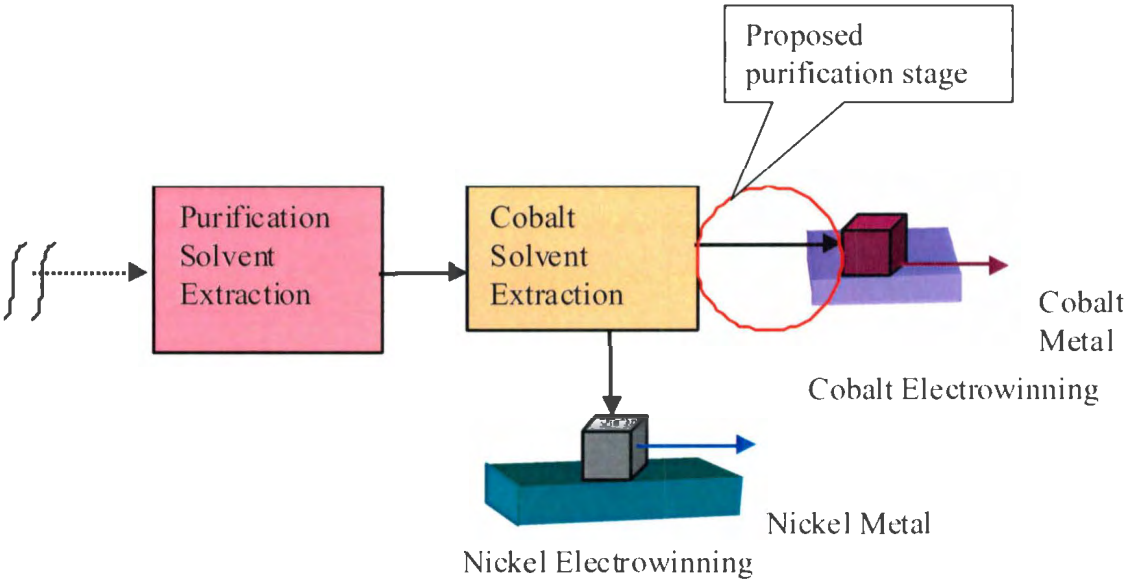


Figure 1.6 Partial flow diagram of Vale Inco's Hydromet process showing proposed purification stage

1.11 Thesis Report

This thesis includes several chapters as mentioned below:

Chapter one gives a through literature search and introduction to the separation and purification process especially extraction aspect of manganese and cadmium from the cobalt electrolyte solution. It also includes the background to the demand, use and production of cobalt. Overview of the basic principles of solvent extraction and ion

exchange techniques and existing technology on solvent extraction process have also been discussed as well in this chapter.

Chapter two describes the experimental study for the removal of manganese (Mn) from the cobalt electrolyte solution by solvent extraction method.

Chapter three describes the experimental study for the removal of cadmium (Cd) from the cobalt electrolyte solution by solvent extraction method.

Chapter four describes an introduction to the ion exchange (IX) method for the removal of impurities from cobalt electrolyte solution and screening test results of the removal of Mn and Cd impurities using different ion exchange resins. The benefit of future research work on manganese removal using IX method has also been discussed in this chapter.

Chapter five describes the discussion on the organic losses issues in SX process and conclusion of the overall study.

CHAPTER 2

Removal of Manganese from Cobalt Electrolyte Solution by Solvent Extraction (SX) Method

2.1 Introduction

The lab experiments were conducted in the Hydrometallurgy Laboratory at memorial University of Newfoundland. The hydrometallurgical process is adopted to remove manganese from the cobalt electrolyte solution (real plant solution generated at Vale Inco's demonstration plant at Argentia, NL, Canada).

During pressure leaching of nickel sulphide ore/concentrate, in addition to nickel (Ni) and cobalt (Co), other metals that are present in the ore/concentrate are also dissolved in the leach liquor. These additional metals form impurities in the electrolyte solution. Over time, these impurities can accumulate in the circuit. To produce pure cobalt, as well as to optimize the process, those impurities must be removed. It was found that the cobalt electrolyte solution generated at Vale Inco's Hydromet Demonstration Plant in Argentia, Canada, contains high tenor cobalt (~90 g/L) with trace amount of copper (Cu), cadmium (Cd), iron (Fe), manganese (Mn), magnesium (Mg), lead (Pb), and zinc (Zn). The physical and chemical properties of the cobalt electrolyte solution are provided in Table A.1 in appendix.

The presence of small amounts of manganese can minimize the corrosion rate of the anodes and the electrowinning of cobalt may require some manganese to minimize the oxidation of Co(II) to Co(III) at the anode (Feather et al., 1999), but excess manganese results in significant decreases in the current efficiency by reducing the current density. Metal deposition rate during electrowinning is greatly dependent on current density (Miousse, 2009). However, excessive hydrogen and oxygen evolution at the cathode and anode respectively decrease current efficiency, resulting worse deposit quality.

At the anode, Mn(II) in the electrolyte is oxidized to form an unstable Mn(III) which disproportionates (Zhang and Cheng 2007a, Cui et al., 2008 and Feather et al., 1999) to Mn (II) and MnO_2. manganese dioxide (MnO_2) precipitates as sludge in the anode bags that clogs the bag which hinders the current flow and reduce current efficiency. As a result, the anode bags need to be removed from the electrowinning cells for periodic cleaning, which is a laborious job that also hampers the cobalt production. Moreover, if any amount of Mn(III) is recycled back to the solvent extraction circuit with anolyte, it may also oxidize and degrade the organic extractant as Cheng et al. (2000) observed the presence of Mn^{3+} results in organic oxidation and, consequently, emulsion formation. Therefore, manganese from the cobalt electrolyte solution needs to be removed. Solvent extraction methods can be applied to both the separation of target metals as well as the removal of other metal impurities and may offer benefits in terms of both cost and ease of operation. Literature searches revealed that D2EHPA, an organophosphoric acid, is suitable for the extraction of manganese over other impurities (Devi et al., 2000). In another study, NH_4-D2EHPA was used for the extraction of manganese (Hoh et al., 1984).

In the present work, a solvent extraction (SX) method has been proposed to selectively remove manganese from an electrolyte solution that contains a large amount of cobalt. Screening tests were carried out in this study to select a proper extractant for manganese removal. A new concept was applied to remove impurities using modified D2EHPA, after converting its functional group with Co^{2+} ions. Also, Na-D2EHPA was studied to examine its extraction ability. The study was based on the effects of several factors, such as equilibrium pH, extraction time, and extractant concentration. A significant amount of manganese was removed from the cobalt electrolyte solution by solvent extraction in a single stage with di (2-ethylhexyl) phosphoric acid (D2EHPA) preloaded with Co^{+2} ions, which have been described in this chapter.

2.2 Solvent (Extractant, Diluent and Modifier)

Extractant

In this study, D2EHPA [di - (2-ethylhexyl) phosphoric acid] has been identified as a suitable extractant in the screening test, for the selective extraction of manganese over other impurities, such as Cu, Ca and Mg. D2EHPA is a known compound and it can be purchased on the commercial market from a number of sources (King, 1985). Use of a particular concentration of D2EHPA is not critical; however, the factors such as viscosity, solubility, phase separation, structure and valence play important role during the extraction process.

In this study, 100 % pure di-(2-ethylexhyl) phosphoric acid (CAS # 298 – 07 – 7) was used as the extractant in the solvent extraction process. It was supplied by Alfa Aesar, A Johnson Mathey Company. The physical and chemical properties of D2EHPA are given in Table A.2 in the Appendix section. The structure of D2EHPA is shown in Figure 2.1.

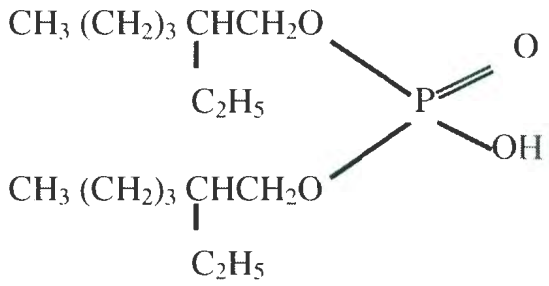


Figure 2.1 Structure of Di- (2-ethylexhyl) phosphoric acid (D2EHPA)

Diluent

Escaid 110 was seleceted as the diluent in this experiment. The selection of a diluent suitable for solvent extraction with D2EHPA was made on the basis of availability and the effect of the diluent on the manganese – cobalt separation.

Modifier

In this study, 100% pure 1-Decanol (CAS # 112 – 30 – 1) was used as the modifier to prevent the third phase formation after solvent extraction process; i.e. to ease the phase separation. It was supplied by Alfa Aesar, A Johnson Mathey Company. The physical and chemical properties of 1-Decanol are provided in Table A.3 (Appendix).

2.3 EXPERIMENTAL

2.3.1 Materials / Reagents

The organic extractant, di (2-ethylhexyl) phosphoric acid (D2EHPA), was purchased from Alfa Aesar (100% pure) and used in this experiment without further purification. The chemical formula of this acidic extractant is $[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2POOH$. In this study, the organic solution was prepared by diluting the extractant in Escaid 110, which is a commercial aliphatic kerosene donated by Univar Canada Ltd., and 1-decanol was used as the phase modifier. An example for the preparation of 20 mL of 25 vol.% D2EHPA is :

1 mL 1 - Decanol and 5 mL D2EHPA was taken in a 20 mL volumetric flask which was filled with Escaid 110 upto its mark.

In the screening tests, some other extractants such as Cyanex 301, Cyanex 923, Cyanex 272, Acorga M5774, Acorga M5640 and Acorga M5510 were used. In all experiments, the real plant solution from Vale Inco's Demonstration Plant at Argentia was used as the aqueous feed solution (hereinafter referred to as "cobalt electrolyte solution"). The analysis of the cobalt electrolyte solution has been discussed in the respective experimental section.

To modify the functional group of D2EHPA with sodium (Na^+) or cobalt (Co^{2+}) ions, a synthetic aqueous solution was prepared by dissolving either NaOH pellet or the salt of cobalt sulphate heptahydrate ($CoSO_4.7H_2O$) in de-ionized water. Reagent grade

hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to control the pH of the solution. Sodium hydroxide (NaOH), also known as caustic soda, is an inorganic compound and strongly alkaline. In this experiment, pellets of NaOH were used to prepare the solution of the required concentration of NaOH. Sodium hydroxide is widely used wherever a strong base is needed, e.g. for the treatment of acidity. It dissolves in water with liberation of heat.

Figure 2.2 below shows a picture of samples of sodium hydroxide and cobalt sulphate heptahydrate used during the experiments of this study.

Figure 2.2: Sodium hydroxide pellets (left) and cobalt sulphate heptahydrate (right)

Cobalt sulphate heptahydrate ($CoSO_4.7H_2O$) used in this study was supplied by Alfa Aesar, A Johnson Mathey Company. The physical and chemical properties of cobalt sulphate heptahydrate ($CoSO_4.7H_2O$) are shown in Table A.4 (Appendix).

2.3.2 Analysis of Cobalt Electrolyte Solution

Actual Plant solutions from Vale Inco's Demonstration Plant at Argentia were collected to investigate the removal of manganese and other impurities from the cobalt electrolyte solution by the SX method. The pH of the aqueous solution was found to be 2.96 and measured by an Orion pH meter (shown in Figure 2.3) at room temperature and calibrated with a buffer solution of a standard pH before its use in each experiment. The pH meter was coupled with the temperature probe.

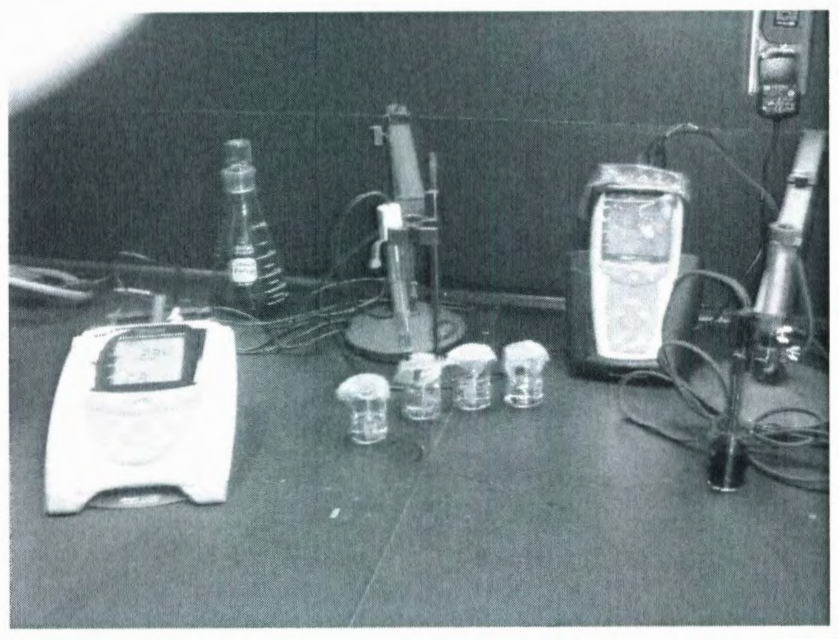


Figure 2.3 Orion pH meter

The concentrations of manganese and cobalt in the feed electrolyte solution were determined using PerkinElmer ELAN DRCII ICPMS (Inductively Coupled Plasma Mass Spectrometry). The lower detection limit during metal analysis by ICPMS for Mn and Co was 0.484 ppb and 9.70 ppb, respectively (Appendix - E4). The results of the concentration of the cobalt electrolyte solution were not constant throughout the

experiment, and they varied with respect to the time of use from stock and calculations for the concentrations of metals after extractions were done accordingly.

2.3.3 Extraction Experiments

Equal volumes of the two phases of known concentrations were shaken at 25 ^{o}C, unless otherwise stated, to measure the equilibrium distribution of metals between the aqueous and organic phases during solvent extraction. All the tests were conducted in an air bath shaker (Innova-43 Incubator Shaker Series from New Brunswick Scientific) with a controlled environment, such as controls on temperature, time and shaking speed (except the kinetic study which was done in a magnetic stirrer). The shaking speed was maintained at 300 rpm with a shaking time that varied from 6 ~ 10 hours to attain equilibrium. A centrifuge (Eppendorf Model: 5810, shown in Figure 2.4) was used to remove any trace amount of emulsified organic from the aqueous raffinate. After the separation of the two phases, the metal concentration in the raffinate was measured by ICP-MS. The metal concentration in the organic phase was calculated from the difference in metal concentrations in the aqueous feed and the raffinate solution.

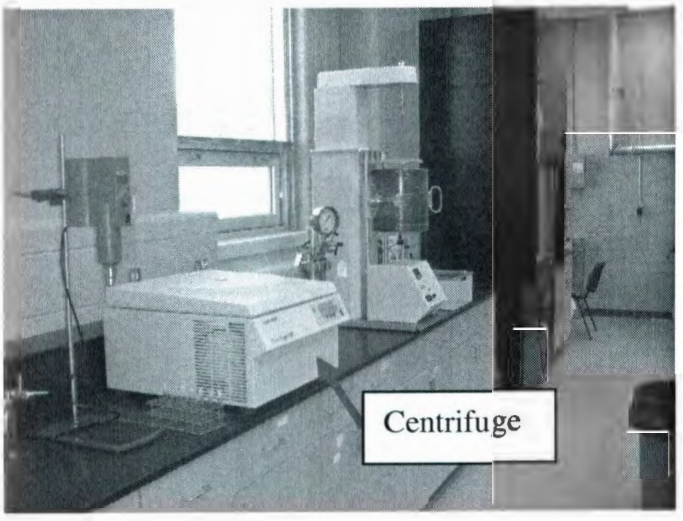
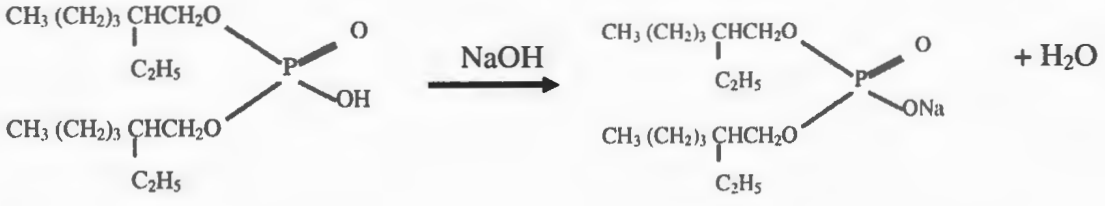


Figure 2.4 Centrifuge machine (Eppendorf Model: 5810)

2.3.4 Preparation of Na-D2EHPA

Na-D2EHPA was prepared by converting the functional group of D2EHPA with sodium ion (Na^+). 40 mL of 0.75 M NaOH solution was shaken with 30 mL of D2EHPA (various concentrations) in an air bath shaker at 25 °C and 200 rpm for 13 hrs. The organic was then separated, and centrifuged to get Na-D2EHPA as shown below in Eq. 2.0.



D2EHPA **Na-D2EHPA**

..... (2.0)

2.3.5 Preparation of Co-D2EHPA

Co-D2EHPA was prepared by pre-loading cobalt ion (Co^{2+}) into D2EHPA. This was done by mixing a 200 mL cobalt sulphate synthetic solution (prepared by dissolving $CoSO_4.7H_2O$ salt in de-ionized water) with 150 mL of D2EHPA (25 vol.%) in a magnetic stirrer. The equilibrium pH of the solution was varied from 3.0 ~ 6.7 to determine the maximum loading of cobalt in D2EHPA. The organic was then separated, and centrifuged to get Co-D2EHPA. The experiment of co-preloading in a magnetic stirrer is shown in Figure 2.5. The extraction details using the Co-D2EHPA as an extractant are described in section 2.4.

Figure 2.5 Co-preloading [aq feed: 22878 ppm Co., org. feed: 25 vol. % D2EHPA]

2.3.6 The Viscosity of Cobalt-Loaded Organic Solution

In the present study, it was found that, when the loading of cobalt reached the maximum stoichiometric value, the viscosity of the organic phase became high. The viscosity increased with the loading of cobalt, but not measured in absolute terms. It was, however, observed visually.

2.3.7 Third Phase Formation in Cobalt-Loaded Organic

In this study, third phase formation was not observed during any of the extraction experiments.

2.4 RESULTS AND DISCUSSION

2.4.1 Screening Tests

The screening tests were carried out with different kinds of extractants to select a suitable extractant for the selective removal of manganese from the cobalt electrolyte solution. The results of the screening tests are summarized in Table 2.1. It was found that D2EHPA had the highest affinity to manganese ions, and 24% manganese was extracted from the cobalt electrolyte solution. However, the pH of the feed solution dropped from 2.94 to 1.94 because of transferring hydrogen ions, that were liberated from D2EHPA during the extraction, for which the extraction of manganese was low at lower pH. The

use of an alkali salt of D2EHPA helps maintain the pH of the solution. At high pH, cobalt is co-extracted. This is expected since Cole (2002) observed that the ideal condition for optimum cobalt extraction was in between pH 5 – 6. Cook and Szmokaluk (1971) suggested that D2EHPA salts of Na, Ca or NH_4 provides a convenient method of controlling pH of the raffinate, and they found that the sodium salt of D2EHPA selectively separates manganese from cobalt. As a first step in this study, screening tests with different extractants were carried out to find out the selective extractant for the extraction of desired metals. The parameters used in the screening test, and the results of the screening test are tabulated in Table 2.1.

Table 2.1 Screening tests results for the extraction of manganese by different extractants

[Feed pH = 2.94, Org. conc. = 20 vol.%, Temp = 25 °C, Time = 25 min.]

Name of Extractant (20 vol.%)	**A/O Ratio**	**Mn conc. in feed solution (ppm)`**	**Mn conc. in raffinate (ppm)**	**% Extraction of Mn**
Cyanex 301	1	742	710	4.3
Cyanex 923	1	742	724	2.4
Cyanex 272	1	742	687	7.4
Acorga-M5774	1	742	720	3.0
Acorga-M5640	1	742	722	2.7
Acorga-M5510	1	742	710	4.3
D2EHPA	1	742	564	24.0

This data table (Table 2.1) is based on raw data of the metal analysis by ICP-MS as provided in Appendix B1.0 (for Mn conc.), B1.1 (for D2EHPA) & B2 (S-3 to 8 where S-3.....S-8 stands for Cyanex 301.... Acorga- M5510, respectively). Some data values were rounded up to the nearest value for the convenience of calculation.

The comparisons of screening test results for different extractants are also shown in the graphical presentation (Figure 2.6)

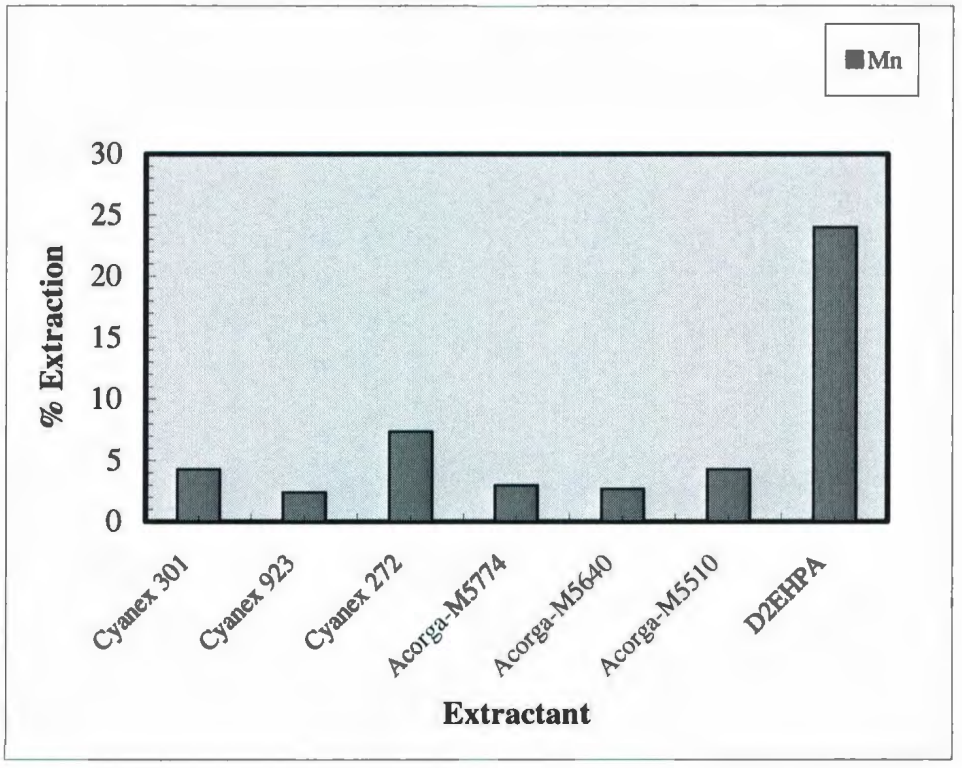


Figure 2.6 Graphical presentation of Mn extraction with different extractants

From the figure of screening test result, it can be seen that D2EHPA had the highest affinity for the extraction of manganese compared to the other extractants. In this study, a new approach of removing manganese from the cobalt electrolyte solution was also applied, where manganese was selectively removed, using cobalt loaded D2EHPA. The

scoping test results are shown in Table 2.2, where it was observed that about 38 % manganese was extracted at pH 1.78 ~ 2.36 by Co-D2EHPA without adding any reagent to control the pH. Solvent extraction with Co-D2EHPA was first carried out in an air bath shaker where the cobalt loading was not seemed to be sufficient (as seen the lower extraction in Table. 2.2).

Table 2.2 Extraction of Mn and Co with varied concentration of Co-D2EHPA [Feed (Co-electrolyte– Appendix B4): $[Mn]_F$ = 674.59 ppm, $[Co]_F$ = 47068.00 ppm, Temp = 25 °C, Time = 1 hr.]

Co-D2EHPA (vol.%)	A/O Ratio	Mn conc. in raffinate, $[Mn]_R$ (ppm)	Co conc. in raffinate, $[Co]_R$ (ppm)	% Mn Extraction	% Co Extraction
5	1	603.57	46678	10.53	0.80
10	1	548.44	44940	18.70	4.50
15	1	527.79	47077*	21.76	-
20	1	479.54	45544	29.00	3.20
25	1	419.93	43501	37.75	7.50

** Indicates error value, because conc. of Co in the raffinate can not be greater than feed conc. of Co in the present system. Extraction will be 'zero' if both amounts are same. But it is not realistic from the measurements performed by any instrument, such as ICP-MS.*

The data table (Table 2.2) is prepared extracting data from the metal analysis report provided in APPENDIX B4 (SX-R-2-1 to SX-R-2-5 that corresponds to the data for 5% – 25% D2EHPA, respectively)]. Extraction (%) of Mn and Co was calculated as follows:

$$\% \text{ Mn Extraction} = \frac{[Mn]_F - [Mn]_R}{[Mn]_F} \times 100 \text{ and}$$

$$\% \text{ Co Extraction} = \frac{[Co]_F - [Co]_R}{[Co]_F} \times 100$$

Where, [Mn] and [Co] denote the concentration of manganese and cobalt in the respective aqueous solutions.

The cobalt pre-loading into D2EHPA could not be controlled at the required level due to inconvenience of adding NaOH solution into the air bath shaker to increase the pH as required. Later, the Co-preloading into D2EHPA was accomplished in a magnetic stirrer, and satisfactory cobalt preloading into D2EHPA was achieved (Table 2.4). Extraction study was carried out using this Co-loaded D2EHPA, which is described in section 2.4.3. To find a comparative study, D2EHPA was also loaded with Na^+ ions and the extractions of metals were carried out with Na-D2EHPA which is discussed in section 2.4.2.

2.4.2 Extraction of Manganese with Na-D2EHPA

It was also found from literature searches that some authors investigated Na-D2EHPA to extract metals from aqueous solutions. In this study, Na-D2EHPA was also used, and attempted to extract Mn. The purpose of the study was to compare the extraction results of Mn with that of Co-D2EHPA, for particular experimental conditions. The results of the extraction of Mn and Co using Na-D2EHPA are provided in Table 2.3.

Table 2.3 Extraction Mn and Co with different concentration of Na-D2EHPA [Feed (Co-electrolyte – 2, – Appendix B5): $[Mn]_F$ = 760.17 ppm, $[Co]_F$ = 55668.00 ppm, Temp = 25 °C, Time = 1 hr.]

Na-D2EHPA (vol.%)	A/O Ratio	Raffinate pH	Mn conc. in raffinate (ppm)	Co conc. in raffinate (ppm)	% Mn Extraction	% Co Extraction
5	1	6.04	424.60	50278	44	10
10	1	5.99	390.38	52278	49	6
15	1	6.25	286.51	47996	62	14
20	1	6.51	220.61	42707	71	23
25	1	6.61	198.80	39996	74	28

This data in Table 2.3 is extracted from the metal analysis raw data table provided in Appendix B5 where samples SX-5-2.1 to SX-5-2.5 correspond to 5% – 25% D2EHPA, respectively in the above table. The concentrations of cobalt were very high compared to

that of Mn concentrations, and that is why, when rounded up to the nearest value, there was no significant effect on the result of cobalt extraction.

Figure 2.7 shows the extraction (%) of manganese and cobalt versus concentration (vol. %) increasing from 5 vol.% to 25 vol. %. The data results were plotted using MS Excel. From the figure it can be seen that the extraction of Mn and Co increased with the increase of organic concentrations, when Na-D2EHPA was used as the organic. The extraction of manganese was found to be 74% with 25 vol.% Na-D2EHPA, however, 28% cobalt was also co-extracted with this extractan, as it can be seen from the significant R^2 value of linear relationship (Figure 2.7). In statistics, R^2 value represents the reliability of linear relationship between dependent and independent variables. As per objective of this study, extraction of manganese was desired with minimum co-extraction of cobalt. In this experiment, co-extraction of cobalt happened as the equilibrium pH of the aqueous solution was high (pH = 6) because of transferring Na^+ ion from Na-D2EHPA into the aqueous solution. Later, this high pH was avoided by the use of Co-D2EHPA as described in the following section.

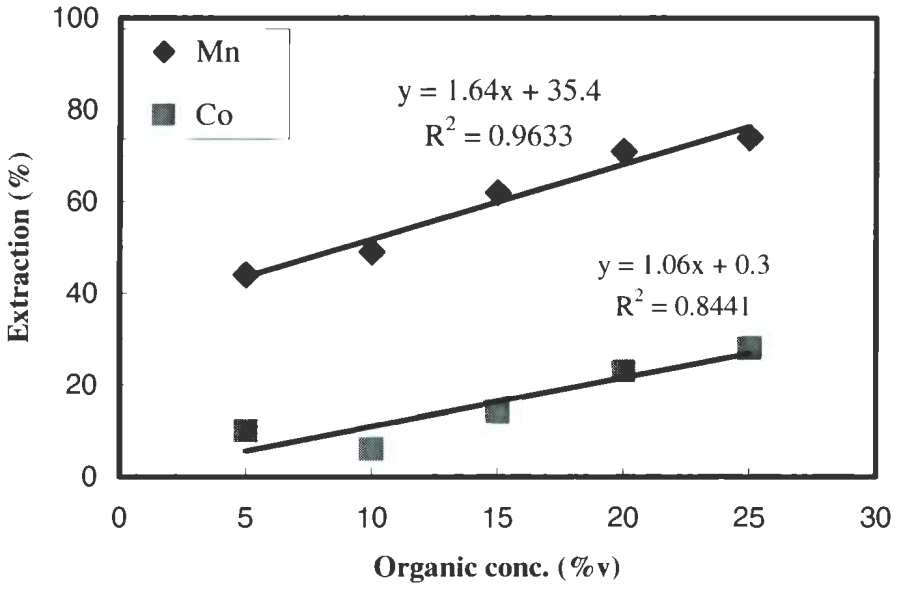


Figure 2.7 Mn and Co extr. with different conc. of Na-D2EHPA at pH around 6

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2.4.3 Extraction of Manganese with Co-D2EHPA

The extraction of metals can not be achieved at the desired level using D2EHPA alone, as mentioned before. This happens due to the drop of equilibrium pH of the solution by transferring the H^+ ions into the solution from D2EHPA. As the Mn extraction is pH dependent, conversion of D2EHPA is necessary to maintain a particular equilibrium pH. In this experiment, D2EHPA was converted by Co^{2+} ions and data on the preparation of Co-D2EHPA is provided in Table 2.4. The preloading of Co^{2+} in D2EHPA was conducted in an open beaker, placed on a magnetic stirrer, and carried out at room temperature. The concentration of cobalt in the synthetic cobalt sulphate solution (feed) was 22876 ppm ($CoSO_4$-syn-Appendix B5) and the concentrations of cobalt in the

raffinate solutions with respect to the different extraction pH were measured by ICP-MS. The pH was increased using 0.75 M NaOH solution. The concentration of cobalt in the organic phase was measured by the difference in concentration of cobalt in the feed solution and the raffinate (after extraction). Considering the results of extractions as well as the inventory cost of organic (extractant), 25% concentration of extractant was selected for further experiments of this study. It was assumed that higher concentration will not bring enough extraction benefit rather it would increase the cost.

Table 2.4 Co preloading in 25 vol.% D2EHPA at different extraction pH

Item no.	Equilibrium pH	Conc. of cobalt in feed (synthetic sol.) (ppm)	Conc. of cobalt in raffinate after preloading (ppm)	% Co loaded
1	3.00	22876	16143	29
2	3.67	22876	12158	47
3	4.05	22876	9944	57
4	4.48	22876	6941	70
5	5.16	22876	4917	79
6	5.91	22876	2642	88
7	6.70	22876	2292	90

Table 2.4 is extracted from the metal analysis raw data table provided in Appendix B5 where T#1 ~ T#7 respectively corresponds to item no. 1 ~ 7 in the above table. Some data values were rounded up for the convenience of calculation however, there were no significant effect on the results for this small change.

The extraction data of cobalt were plotted against extraction pH using MS Excel, where the best fit of data were found with polynomial model equation of order 2 and with significant R^2 value (= 0.9958) as given in the figure 2.8.a.

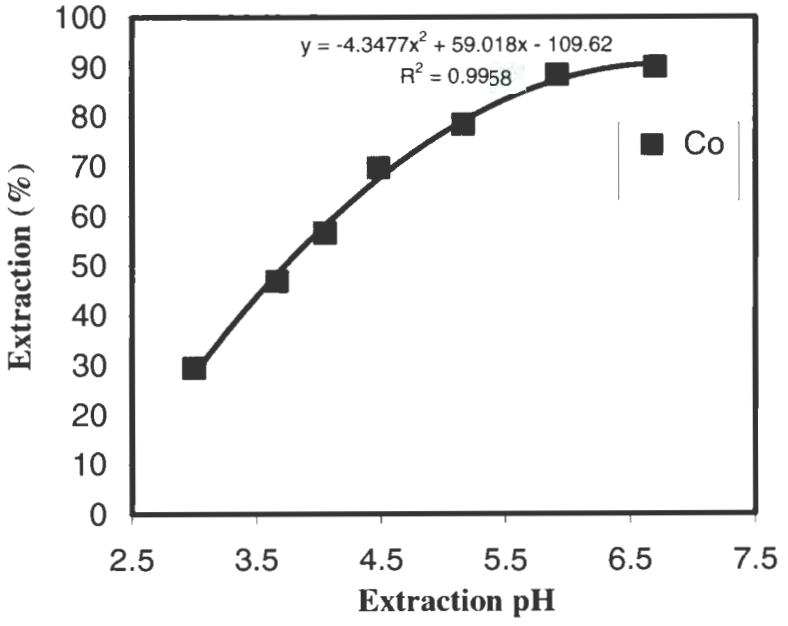

Figure 2.8.a Co preloading in 25 vol.% D2EHPA at different extraction pH

Practically it was found that when extraction pH crosses 6.5, the precipitation of cobalt started, that is why, higher pH (>6.5) was not suitable for cobalt preloading. Considering this aspect, first 6 data points were selected and plotted again (Figure 2.8.b), where it was seen that the cobalt loading showed linear relation ship with extraction pH upto around 6 as it is significant with R^2 value (= 0.968) of trend line (Figure 2.8.b). Cobalt was not extracted linearly beyond this value, rather the precipitation was observed which was not desirable.

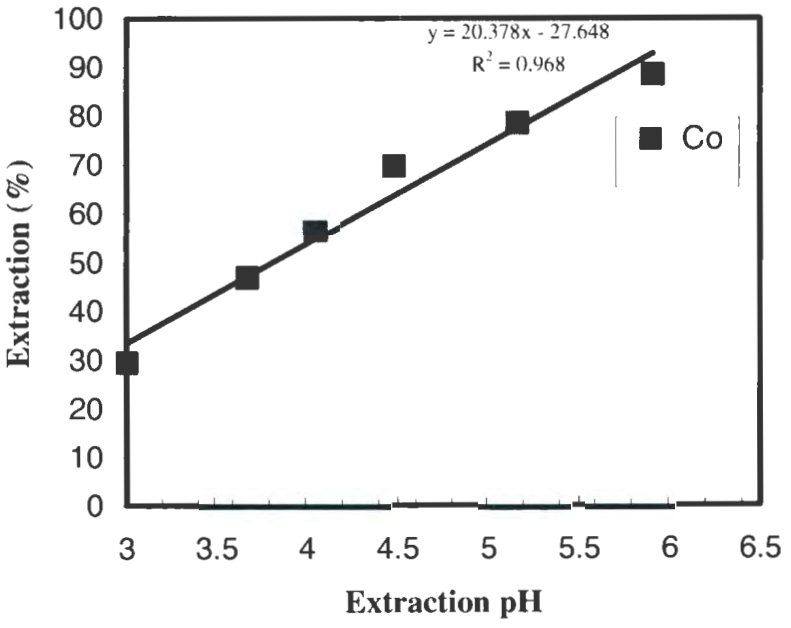

Figure 2.8.b Co preloading in 25 vol.% D2EHPA at different extraction pH (considering first 5 points: pH 3 ~ 6)

From the results, it was found that around 90% cobalt was extracted nearby pH 6, which would be the suitable pH for the cobalt pre-loading in D2EHPA. This pre-loaded D2EHPA, which is called Co-D2EHPA, is then used in the solvent extraction process, for the removal of impurities from the cobalt electrolyte solution. Extraction results are presented in Table 2.5.

Table 2.5 Extraction of Mn and Co with 25 vol.% Co-D2EHPA

[Feed (Co-elect-2 - Appendix B5): Mn = 760.17 ppm and Co = 55668.00 ppm , Org. = 25 vol.%, Temp = 25 °C,Time 2 hrs.]

Raffinate pH	A/O Ratio	Mn conc. in raffinate (ppm)	Co conc. in raffinate (ppm)	% Mn Extraction	% Co Extraction
3.5	1	218.23	55390	71.3	0.5
3.8	1	214.84	55176	71.7	0.4
4	1	193.3	51515	74.6	7.4
4.9	1	161.85	48532	78.7	12.8
5.4	1	166.82	49877	78.0	10.4

This data table (Table 2.5) is prepared from the metal analysis raw data provided in Appendix B5 where samples SX-R3.1 to SX-R3.5 correspond to the data for pH values 3.5 ~ 5.4 respectively in the above table.

Table 2.5 shows the results of the extraction of metals with Co-D2EHPA, where it was found that 70 – 80% manganese was extracted within the pH range of 3.5 – 5.5. The extraction percentage was drastically improved by controlling the equilibrium pH of the solution. The results of the extraction of Mn and Co versus raffinate pH have been shown in Figure 2.9 where it can be found that the co-extraction of cobalt was negligible at pH 3.5. However, about 10% cobalt was extracted at pH greater than 5.

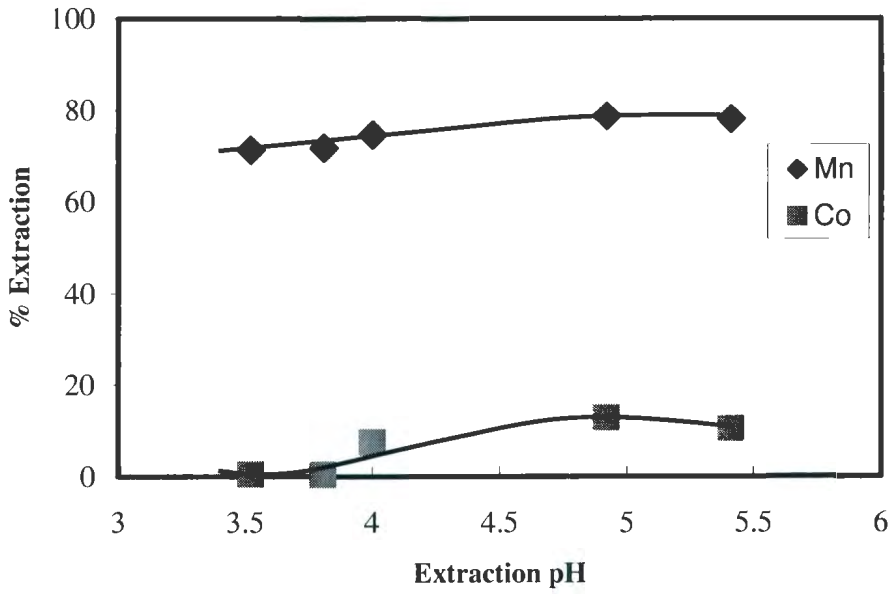

Figure 2.9 Mn and Co extraction at different pH range with 25 vol.% Co-D2EHPA

From Figure 2.9, it also can be seen that more than 70% manganese can be removed at around pH 3.5 without losing any cobalt in the impurities removal stage. This would be a suitable condition for the selective removal of manganese from the cobalt electrolyte solution. Further increase in pH will result significant co-extraction of cobalt. It was not an objective to extract 100% Mn from cobalt electrolyte solution, as small quantity of Mn in the solution is useful for the process as discussed earlier. The time allotted in this experiment was more than that of with Na-D2EHPA to observe the co-extraction of cobalt, as the equilibrium of cobalt extraction was found slower (as shown later in the kinetic study of this research) than manganese.

Application of Co-D2EHPA which was investigated in this study was new for the removal of manganese from the cobalt electrolyte solution. The advantages of using Co-D2EHPA were:

1) During extraction only Co^{2+} ion was transferred into the cobalt electrolyte solution rather than transferring H^+ or Na^+, and hence it was easy to control the pH of the solution at the desired level.
2) Manganese was selectively removed at pH 3 – 4 without losing any cobalt through co-extraction.

Cheng (2000) carried out study on the separation of manganese from cobalt and nickel, using D2EHPA in kerosene, and found that temperature and pH had significant effects on the extraction. The author reported that at 23°C and pH 3.5, the separation of manganese from cobalt was better however, the separation of manganese from nickel required elevated temperatures (40 – 60 °C). Hoh et al. (1984) studied separation of manganese from cobalt by D2EHPA where the effects of organic pH on manganese and cobalt extraction were investigated with the aqueous feed pH in the neighborhood of 4.2. It was also reported that poor separation efficiency was obtained when organic pH >4, and it happened due to the small separation factor between two metals. Separation factor (as shown in Figure 2.10) in this study provided more favorable results of the extraction of manganese from cobalt (without losing any cobalt through co-extraction) at equilibrium pH 3.5, using the extractant Co-D2EHPA.

2.4.4 Distribution Ratio and Separation Factor in Solvent Extraction

Distribution ratio: The distribution ratio is the ratio of metal concentration in the organic phase and aqueous phase.

Selectivity of a desired metal ion is frequently the key to the success of the solvent extraction process. The selectivity is often described using the term distribution ratio. The distribution ratio D is defined by Eq. 2.1 below

$$D = \frac{(w - w_1) / V_o}{w_1 / V_a} \quad \text{.....(2.1)}$$

where, w represents the original weight of the solute in the aqueous phase and w_1 represent the final weight of the solute in the aqueous phase, Vo and Va are the volume of organic and aqueous solution respectively. Rearranging eqn. 2.1 will yield,

$$\frac{w_1}{w} = \frac{Va}{VoD + Va} = \frac{1}{1 + D(Vo/Va)} \quad \text{.....(2.2)}$$

Since percent extraction can be described by

$$\% \text{ Extraction} = \frac{w - w_1}{w} \text{ X } 100 = [\,VoD/(VoD + Va)\,] \text{ X } 100 \quad \text{.....(2.3)}$$

When solvent extraction takes place in series, the following analysis is valid:

In the first tank, the final weight of the solute w_1 would have the following expression, according to Eq. 2.2,

$$w_1 = w\left[\ \frac{1}{1 + D(Vo/Va)}\ \right] \quad \text{.....(2.4)}$$

The final weight in the second tank could be expressed similarly,

$$w_2 = w_1\left[\ \frac{1}{1+D\left(Vo/Va\right)}\ \right] \quad \text{.....(2.5)}$$

$$= w\left[\ \frac{1}{1+D\left(Vo/Va\right)}\ \right]^2 \quad \text{.....(2.6)}$$

And, for the nth tank, the final weight of the solute, w_n, could be evaluated as

$$w_n = w\left[\ \frac{1}{1+D\left(Vo/Va\right)}\ \right]^n \quad \text{.....(2.7)}$$

In this way, the ultimate recovery of metal ions in the nth tank can be calculated using Eq. 2.8 below,

$$\%\ \text{Extraction} = \left[\ 1 - \frac{w_n}{w}\ \right] \text{X } 100 \quad \text{.....(2.8)}$$

Separation factor: The separation factor for two metal ions for example Mn and Co is the ratio of their distribution coefficients ($\beta = D_{Mn}/D_{Co}$) i.e.

$$\beta = \frac{D_{Mn}}{D_{Co}} = \frac{\dfrac{[Mn]_{org}}{[Mn]_{raff}}}{\dfrac{[Co]_{org}}{[Co]_{raff}}} = \frac{[Mn]_{org}[Co]_{raff}}{[Mn]_{raff}[Co]_{org}} \quad \text{.....(2.9)}$$

under identical experimental conditions.

2.4.5 Results of Calculation for Separation Factor (S.F.) of Manganese and Cobalt

Distribution ratio and separation factor of Mn and Co were calculated using equation 2.1 and 2.9, respectively and presented in Table 2.6.

Table 2.6 Separation factors of Mn and Co with different equilibrium pH [Org. = 25 vol.% D2EHPA in Escaid 110, O/A = 1, Temp. = 25 °C, $[Mn]_F$ = 760 ppm, $[Co]_F$ = 55668 ppm, $[pH]_F$ = 2.94, $D_{Mn} = [Mn]_O/[Mn]_A$, $\beta_{Mn\text{-}Co} = D_{Mn}/D_{Co}$]

Solution item	Equilibrium pH				
	3.5	**3.8**	**4**	**4.9**	**5.4**
$[M_n]_A$ (ppm)	218	215	193	162	167
$[M_n]_O$ (ppm)	542	545	567	598	593
D_{Mn}	2.49	2.53	2.94	3.69	3.55
$[Co]_A$ (ppm)	55390	55176	51515	48532	49877
$[Co]_O$ (ppm)	279	492	4154	7136	5791
D_{co}	0.005	0.009	0.081	0.150	0.120
S. F. $\beta_{Mn\text{-}Co}$	498.00	281.11	36.30	24.60	29.58

In the above table, subscripts 'F' stands for the feed solution and 'A' stands for aqueous (raffinate). The concentrations of Mn and Co were rounded up to the nearest numbers to avoid the more decimals for the value of distribution ratio. The raw data table is provided in Appendix B5. A sample calculation for the distribution ratio and the separation factor of Mn and Co (at pH 3.5) is shown in Appendix C1.

The effects of equilibrium pH on the separation factors of Mn and Co is shown in Figure 2.9 where it can be seen that at lower pH, separation factor for Mn and Co is maximum. With the increase of equilibrium pH, the separation factor decreased significantly.

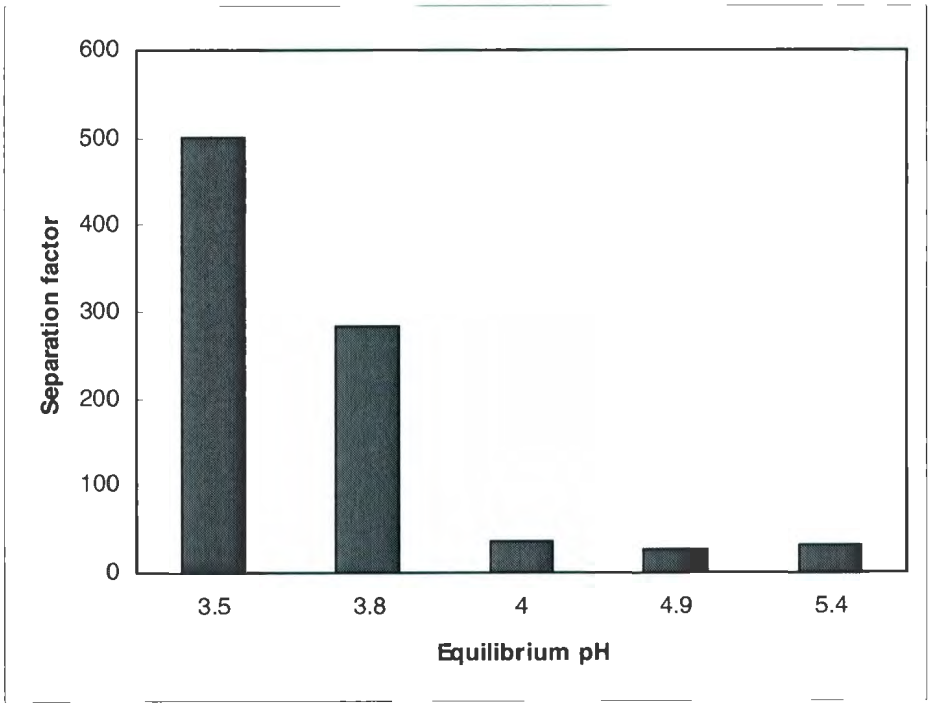

Figure 2.10 Effect of equilibrium pH on Separation Factor of Mn and Co

The choice of equilibrium pH is important for the extraction of metals of interest, as the extractions are pH dependent. As shown in Figure 2.10, the separation factor is maximum at pH 3.5 and this would be the suitable condition for the extraction of manganese using Co-D2EHPA without or minimum co-extraction of cobalt. It was also observed that the separation factor of manganese over cobalt was lowest at pH 4.9, as there was a significant co-extraction of cobalt at this pH.

2.4.6 Kinetics of Manganese Extraction

It is important to investigate the kinetics of metal extraction i.e. rate at which the solute is transferred between the two phases. The contact time of two phases is important to predict the degree of separation in the solvent extraction techniques. The kinetics of the metal extraction were carried out for finding the time required for the extraction equilibrium of manganese, and the results are presented with a plot in Figure 2.11. The experiments of extraction kinetics were conducted using Na-D2EHPA and Co-D2EHPA in an open beaker placed on a magnetic stirrer, where the solution was continuously stirred. It was found from a study (Biswas and Mondal, 2003) that the extraction equilibrium of manganese could be attained faster by vigorous shaking however, there is a chance of the entrainment of organic into the aqueous phase. In the present experiments of kinetic study, Mn conc. in the aqueous feed was 732.56 ppm and that of cobalt was 50335.08 ppm [Co-elect-2: Appendix B6]. Organic used in this experiment was 25 vol. % Na-D2EHPA. The experiment was conducted at pH 5.5 with A/O = 1 and at temp. 25 ^{o}C. The results of the kinectic study for the extraction of Mn and Co, using 25 vol. % Na-D2EHPA is provided in Table 2.7.

Table 2.7 Results of kinectic study for the extraction of Mn and Co using 25 vol. % Na-D2EHPA

Time (min.)	Conc. of Mn in raffinate (ppm)	Conc. of Co in raffinate (ppm)	Mn extraction (%)	Cobalt extraction (%)
5	186.09	40260.15	74.6	20.02
10	178.21	38723.58	75.67	23.07
60	171.91	33343.19	76.53	33.76
120	178.18	34593.88	75.68	31.27
300	168.21	32891.55	77.04	34.65
600	180.59	35686.58	75.35	29.10

This data table (Table 2.7) corresponds to the 'Mn' and 'Co' column of metal analysis data provided in Appendix B6 (Sample: SK-1 ~ SK-6).

Figure 2.11.a shows the results of the kinetic studies for the extraction of metals with 25 vol. % Na-D2EHPA for the duration of 0 ~ 600 min. It was found that the kinetic for the extraction of manganese was very fast and equilibrium reached within a short time, which was made clear by plotting another graph (Figure 2.11.b) with a shorter time span to show the significance of faster equilibrium for the extraction of Mn. For better resolution of graph a log-log plot is also provided in Figure 2.11.c showing extraction (%) of Mn and Co against time (min.). The the kinetic of cobalt extraction was found slower when compared to that of Mn.

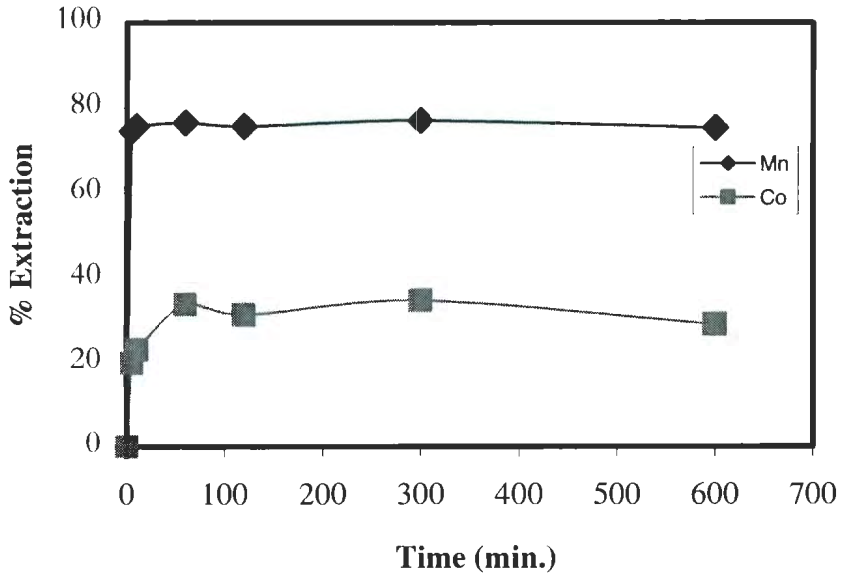

Figure 2.11.a Kinetics of metals (Mn & Co) extraction with 25 vol.% Na-D2EHPA (0 ~ 600 min)

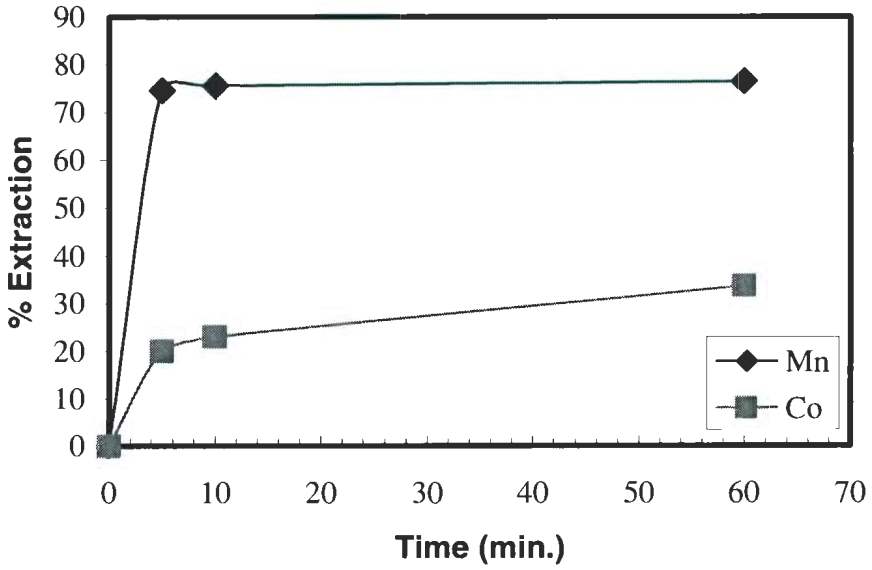

Figure 2.11.b Kinetics of metals (Mn & Co) extraction with 25 vol.% Na-D2EHPA (0 ~ 60 min.)

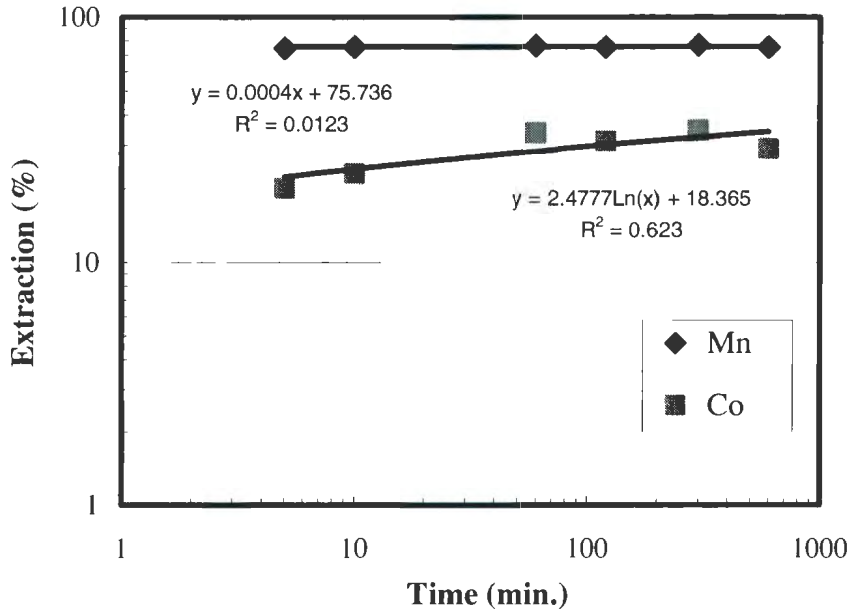

Figure 2.11.c Log-log plot showing the kinetics of Mn and Co extraction with 25 vol. % Na-D2EHPA

Figure 2.11.c was prepared based on the data provided in Table 2.7 (extracted from Appendix B6). The regression for the Mn extraction shows that there is a little correlation with the variation of x-values i.e time constant, and hence can be considered as the equilibrium condition reached for Mn. As can be seen from the figure, the kinetic for the extraction of manganese was very fast and equilibrium reached after around 5 min. of contact time. However, the kinetic of cobalt extraction was not fast, instead, it can be found from the trend line of the log-log plot that there is a significant co-relation with time, and that is why, the extraction equilibrium of Co reached far later. From the experimental results it was observed that based on the difference of the extraction rate, selective separation of manganese over cobalt is possible using Na-D2EHPA.

The study of extraction kinetic using Co-D2EHPA (25 vol. %), with the same experimental conditions was carried out for finding the extraction equilibrium of manganese and the results are presented in Table 2.8.

Table 2.8 Results of kinectic study for Mn and Co extraction using 25 vol. % Co-D2EHPA

[Feed (Co-elect-2): Mn = 732.56 ppm, Co = 50335.08 ppm, Org. = 25 vol.% Co-D2EHPA, pH = 5.5, Temp = 25 °C]

Time (min.)	Conc. of Mn in raffinate (ppm)	Conc. of Co in raffinate (ppm)	Mn extraction (%)	Cobalt extraction (%)
5	156.14	48553.57	78.69	3.54
10	153.55	49762.64	79.04	1.14
60	161.12	51105.94*	78.01	-
120	154.02	47578.13	78.98	5.48
300	156.26	49195.86	78.67	2.26
600	143.71	46612.78	80.38	7.40

*[*Error value, as the concentration of Co in raffinate can not be higher than that of in the feed concentration. Minimum extraction could be zero when there is no co-extraction of cobalt in the organic phase; i.e. concentration of cobalt in the feed and raffinate should be equal. But practically it is difficult to achieve the same measurement for the concentration of any metals in the feed solution and raffinate (after extraction process), using any instrument*].

This data set (Table 2.8) corresponds to the metal analysis report provided in Appendix B6 (Sample: CK-1 ~ CK-6)]

Figures 2.12.a shows the results of the kinetic studies for the extraction of metals, with 25 vol.% Co-D2EHPA for a period of 0 ~ 600 min. It was found that the kinetics for the extraction of manganese was very fast and equilibrium reached within a short time, as found earlier in the case of Na-D2EHPA. The kinetics of the extraction of metals were made clear, plotting another graph (Figure 2.12.b), with a shorter time span, to show the significance of faster equilibrium for the extraction of Mn.

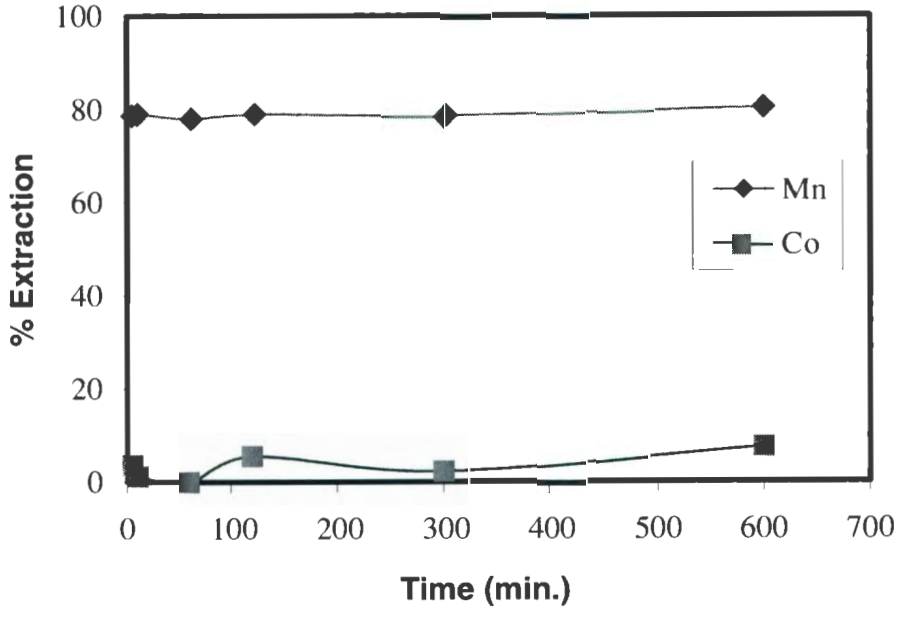

Figure 2.12.a Kinetics of the extraction of metals with 25 vol.% Co-D2EHPA (0 ~ 600 min.) [Feed: Mn = 760 ppm, Co = 55668 ppm, pH = 5.5, A/O = 1]

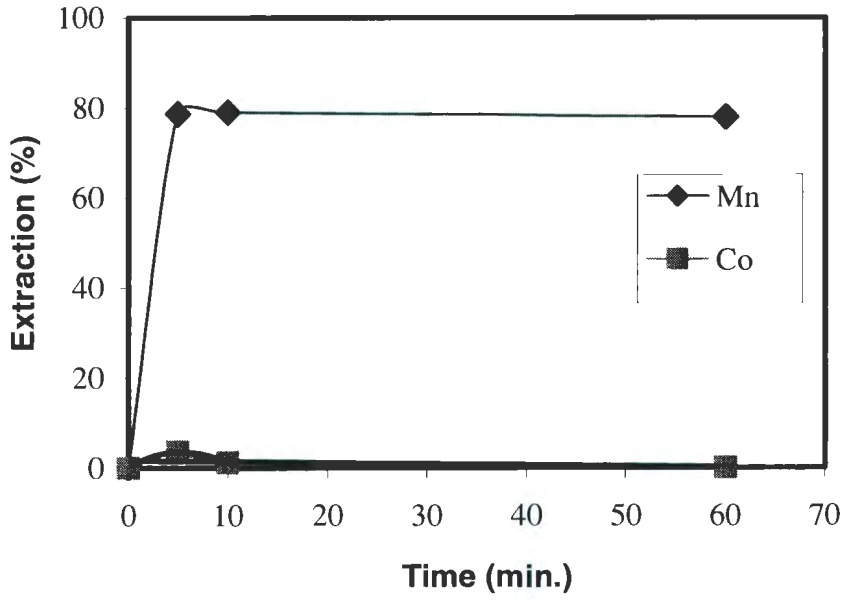

Figure 2.12.b Kinetics of the extraction of metals with 25 vol.% Co-D2EHPA (0 ~ 60 min) [Feed: Mn = 760 ppm, Co = 55668 ppm, pH = 5.5, A/O = 1]

A log-log plot is also provided in Figure 2.12.c showing the better resolution of graphs for the kinetics of the extraction (%) of Mn and Co with respect to time.

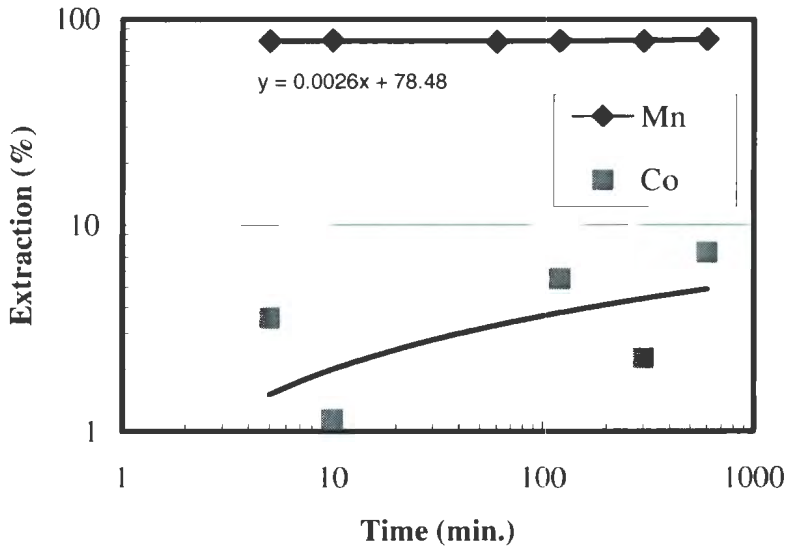

Figure 2.12.c Log-log plot showing the kinetics of Mn and Co extraction with 25 vol. % Co-D2EHPA

As seen from the figure, the kinetic for the extraction of Mn was very fast and equilibrium reached around after 5 min. of contact time. From the trend line, as well as the model equation, it can be seen that, there is a little correlation of Y-values (% extraction) with that of X-values (time) after around 5 minutes, when the equilibrium of Mn extraction reached. On the other hand, the kinetic of cobalt extraction was not faster compared to that of Mn which can be understood through the trend line of the log-log plot. From the above experimental results it was observed that based on the difference of the extraction rate, the selective separation of manganese over cobalt is also possible using Co-D2EHPA.

2.4.7 Stripping of Manganese

In a stripping stage, the loaded metals are extracted back from the organic phase to the aqueous phase. The organic phase may then be treated to reuse. Literature searches revealed that dilute sulphuric acid performed well for the stripping of manganese. Devi et al. (2000) used 0.001 – 0.12 M H_2SO_4 at equal phase ratio and found that more than 97% manganese was stripped from loaded Na-D2EHPA with a concentration of 0.01 M and higher, where the complete extraction took place with 0.1 M sulphuric acid. In the present study, 0.02 M to 1.0 M H_2SO_4 were used to examine the metal stripping from the loaded Co-D2EHPA which is furnished in Table 2.9.

In a batch experiment of this study, 20 mL of loaded organic and 20 mL H_2SO_4 was mixed and shaken in an air bath shaker, with a shaking speed of 300 rpm and at temperature 25 ^{o}C for a period of 2 hrs. It was found that 100% manganese was stripped (Figure 2.13.a) using 0.4 M conc. of H_2SO_4 in a single stage. The pH of the raffinate solution was 1.45. Since sulphuric acid may also strip cobalt from the cobalt preloaded extractant, it is recommended that the stripping be carried out when organic is fully loaded with manganese and other impurities since co-extraction of cobalt is negligible in the specified pH level.

Table 2.9 Stripping results of Mn at different concentration of H_2SO_4

[Loaded Org. Feed: Mn* = 536 ppm, A/O = 1, Temp. 25 °C, Time 2 Hrs.]

H_2SO_4 conc. (M)	Mn conc. in strip solution (ppm)	Sample no. in data sheet	% Stripping of Manganese
0.02	3.04	Str-1	0.55
0.04	6.30	Str-2	1.17
0.06	9.75	Str-3	1.80
0.08	14.24	Str-4	2.60
0.10	17.56	Str-5	3.27
0.20	41.99	Str-6	7.83
0.40	600.26	Str-7	100.00
0.50	689.20	Str-8	100.00
0.80	691.59	Str-9	100.00
1.00	666.40	Str-10	100.00

[*Mn* = Conc. of manganese in organic phase was obtained from the mass balance of Co-electrolyte (feed) and raffinate after extraction and denoted by CF-2 and SXR-2 respectively in the metal analysis data sheet provided in Appendix-B7.2*].

The data table (Table 2.9) is extracted from the metal analysis data provided in Appendix B7.1 & B7.2. It has been observed in the above table that sample # Str-7 ~ Str. 10 shows more concentration than that of manganese concentration transferred into the organic. From the reality of this experiment, the maximum manganese concentration in the raffinate could be 536 ppm. Any concentration higher than that in the raffinate could be assumed as stripped 100% from the loaded organic using. 0.4 M sulphuric acid. For

better resolution of graph log-log plot has been presented (Figure 2.13.b) showing the stripping (%) versus sulphuric acid concentration (M). It shows that 0.4 M or higher concentration can strip 100% Mn from the loaded organic. As higher concentration than 0.4 M sulphuric acid will not bring any benefit for the process and hence it was concluded that 0.4 M sulphuric acid is optimum for stripping of 100% Mn. For the stripping study, the statistical estimate of sensitivity measurements (cps) for the three repetitive standard measurements by ICP-MS (Appendix- E3) is provided in Appendix E (E3.1, E3.2 & E3.3) and all RSD's (relative standard deviation) were found within the acceptable precision limit.

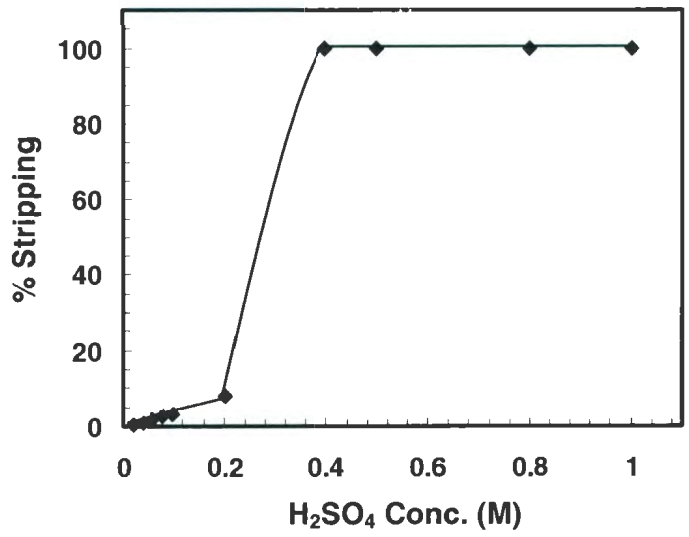

Figure 2.13.a Stripping (%) of manganese at different concentration of H_2SO_4

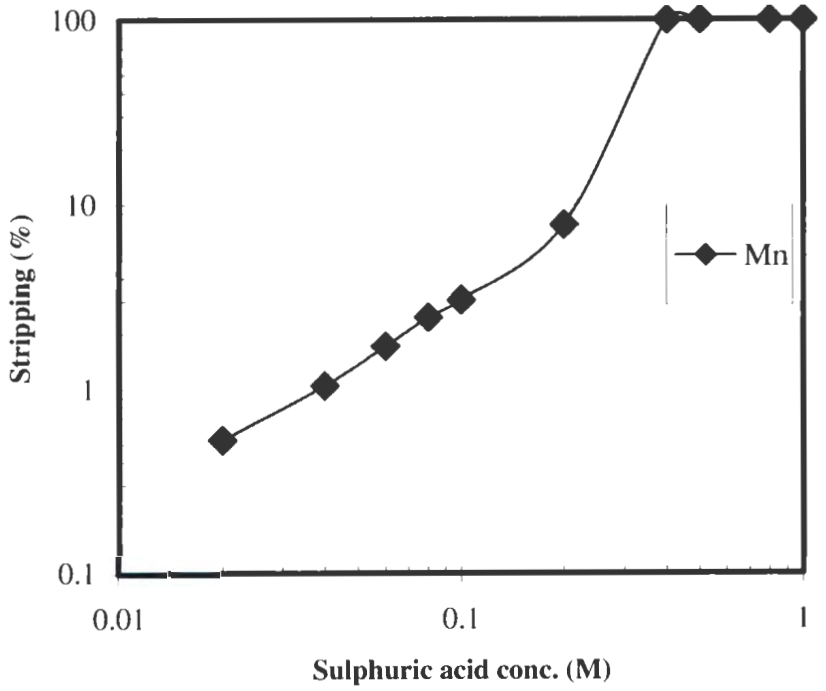

Figure 2.13.b Log-log graph for the stripping (%) of manganese at different concentration of H_2SO_4

2.4.8 Extraction Mechanism

In cobalt electrolyte solution, manganese stays as cationic species as Mn^{2+}. The organic extractant, di-2-ethyl-hexyl phosphoric acid (D2EHPA) is good for extracting the cationic species from the aqueous solution, where hydrogen ion in the extractant is replaced with the metal ion as shown in Equation 2.10. Here, M^{n+} denotes the metal ion, RH is the extractant, and subscripts "org" and "aq" are the organic and aqueous phases, respectively.

$$[M^{n+}]_{aq} + n[RH]_{org} \longrightarrow [MR_n]_{org} + n[H^+]_{aq} \quad \text{.....(2.10)}$$

Na-D2EHPA

Preloading: $[NaOH]_{aq} + [RH]_{org} \longrightarrow [RNa]_{org} + [H_2O]_{aq}$ .....(2.11)

Extraction: $[MnSO_4]_{aq} + 2[RNa]_{org} \longrightarrow [R_2Mn]_{org} + [Na_2SO_4]_{aq}$ .....(2.12)

Co-D2EHPA

Preloading: $[CoSO_4]_{aq} + 2[RH]_{org} \longrightarrow [R_2Co]_{org} + [H_2SO_4]_{aq}$ ..... (2.13)

Extraction: $[MnSO_4]_{aq} + [R_2Co]_{org} \longrightarrow [R_2Mn]_{org} + [CoSO_4]_{aq}$ .....(2.14)

Equations 2.11 – 2.14 show the process reactions in the case of Na-D2EHPA and Co-D2EHPA, where Na^+ and Co^{2+} ions are preloaded into D2EHPA to convert its functional group (Equations 2.11 and 2.13, respectively). Divalent manganese is extracted by converted extractant via a cation exchange mechanism as shown in Equations 2.12 and 2.14.

2.5 Conclusion

A solvent extraction method has been examined to remove manganese from a cobalt electrolyte solution, generated in Vale Inco's demo plant at Argentia, Canada. In this method, manganese was removed from a solution containing large amount of cobalt, using modified D2EHPA. The functional group of D2EHPA was converted to the form of

Na-D2EHPA and Co-D2EHPA by introducing Na^+ and Co^{2+} ions, respectively. The application of Co-D2EHPA for manganese removal from the cobalt electrolyte solution is new and it has several advantages, as mentioned earlier. The experimental results revealed that Co-D2EHPA is superior to Na-D2EHPA, where 70% manganese can be selectively removed from the cobalt electrolyte solution by 25 vol.% Co-D2EHPA at an equilibrium pH of around 3.5, without losing any cobalt through co-extraction. If pH goes over 5, extraction of manganese could be increased to 80%, but a certain amount of cobalt was also be co-extracted, which was not desirable. The kinetics of extraction was very fast and equilibrium was attained within around 5 minutes of contact time. From the metal analysis data (measured by ICP-MS) for the sripping experiments, it was found that the relative standard deviation (RSD) for concentration measurement of Mn, Co and Cd was 4%, 3.4% and 4.4%, respectively which were within the limit of 10% (Appendix E: Table E3.1, E3.2 and E 3.3 for measurement of manganese, cobalt and cadmium, respectively). Xie et al. (2006) found RSD less than 3.6% using high resolution inductively coupled plasma mass spectrometry.

CHAPTER 3

Removal of Cadmium from Cobalt Electrolyte Solution by Solvent Extraction (SX) Method

3.1 Introduction

Cadmium (Cd) is another impurity in the cobalt electrolyte solution which deteriorates the quality of the cobalt product. The cadmium impurity is carried over from the leach solution after dissolving the ore/concentrate in an industrial acid. Sometimes cadmium appears as a minor impurity in cobalt–nickel solutions which can be extracted and removed by solvent extraction method to produce pure cobalt. In this study, at first, screening test was conducted to find out the selective extractant for the extraction of cadmium. Experimental results (Table 3.1) showed that the cadmium can selectively be extracted by D2EHPA when compared to other extractants used in the test. D2EHPA was found to have a significant affinity for the extraction of cadmium from the cobalt electrolyte solution. Cyanex 272 was the second in order and the Acorga-M5640 was the third, while the other extractants showed no extraction for the cadmium.

3.2 Solvent (Extractant, Diluent and Modifier)

Same extractant/diluent/modifier was used in this experiment and with the equal concentration as mentioned in Chapter-2.

3.3 Experimental

3.3.1 Reagent

In this experiment, the real plant solution containing cadmium was used as the aqueous feed solution. The organic extractant, di (2-ethylhexyl) phosphoric acid (D2EHPA) was purchased from Alfa Aesar and was used in this experiment without further purification. The chemical formula of this acidic extractant is $[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2POOH$ and other properties are provided in Appendix A.2.

In this study, the organic solution was prepared by diluting the extractant in Escaid 110, which was a commercial aliphatic kerosene donated by Univar Canada Ltd., and 1-decanol was used as the phase modifier. The NaOH of 0.3 M solutions were used in order to maintain desired equilibrium pH of the solution during extraction.

3.3.2. Procedure

During extraction experiments, equal volume (20 mL) of each of aqueous feed solution and organic extractant either Na-D2EHPA or Co-D2EHPA (preparations were mentioned in the previous chapter) were mixed in a 100 mL Erlenmeyer flask, which was shaken in an air bath shaker (model: Innova-43 – from New Brunswick Scientific) at 300 rpm for a period of 6 hours at 25°C. After equilibration, the phases were allowed to separate and centrifuged using a centrifuge (Ependorf-Model 5810) to remove any trace amount of emulsified organic from the aqueous raffinate. The cadmium in the raffinate solution was

measured by ICP–MS [same test protocol and methods were used as described in chapter-2] and the concentrations of cadmium in the organic was obtained from the mass balance i.e. difference in concentration of cadmium in the feed solution and in the raffinate solution. H_2SO_4 of different concentration were used to strip cadmium from the loaded organic.

3.4 Results and Discussion

As mentioned before, screening test was carried out to find out the selective extractant for the extraction of cadmium from cobalt electrolyte solution. Seven organics were used in the experiments. The concentration of each organic was 20% and concentration of cadmium in the feed solution was 54.78 ppm (Table 3.1 and ICP data sheet at Appendix B1.0). The pH of the aqueous feed solution was 2.94. The experiment was carried out at 25°C and for a period of 25 minutes. The results are shown in Table 3.1.

Table 3.1 Results of the screening tests for the extraction of cadmium by different extractants

Name of Extractant (20 vol.%)	A/O Ratio	Cd Conc. in Feed Solution (ppm)	Cd Conc. in Raffinate (ppm)	% Extraction of Cd
Cyanex 301	1	54.78	ND*	-
Cyanex 923	1	54.78	55.85**	-
Cyanex 272	1	54.78	51.02	6.86
Acorga-M5774	1	54.78	55.22**	-
Acorga-M5640	1	54.78	52.86	3.50
Acorga-M5510	1	54.78	54.73	0.09
D2EHPA	1	54.78	45.63	16.70

** ND- Not Detected*

[*** Error values: The concentration of cadmium in the raffinate can not be higher than that of feed solution*].

The ICP data for the extraction of cadmium is provided in Appendix B1.1 for D2EHPA & Appendix B2 for other extractants (S-3… S-8 stands for Cyanex 301…. Acorga-M5510, respectively). Some data values were rounded up for the convenience of calculation.The results of the screening tests are presented in a graphical presentation as shown in Figure 3.1.

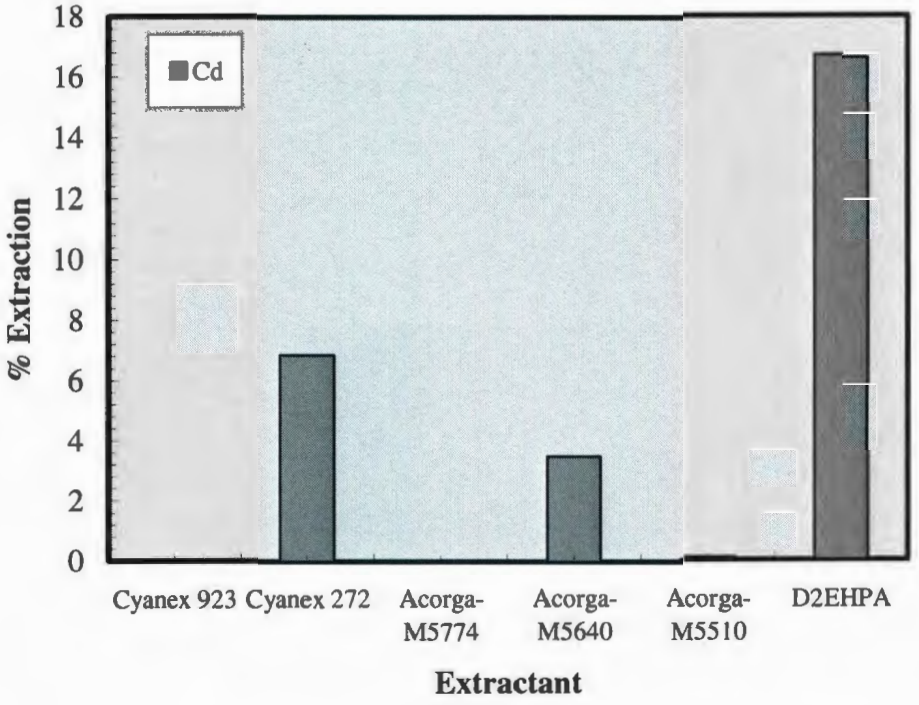

Figure 3.1 Extraction (%) of cadmium by different extractant

Among those extractants, D2EHPA was found to have the highest affinity for the extraction of cadmium. Though the extraction shown in Figure 3.1 was not satisfactory using D2EHPA alone, as a result, D2EHPA was converted by converting its functional group (H^+), with Na^+ and Co^{2+} ions, and the results are discussed in the following sections. In the extraction experiments, converted D2EHPA (Na-D2EHPA and Co-D2EHPA) were used and it was found that a significant amount of cadmium was extracted at pH around 3.5.

3.4.1 Preparation of Na-D2EHPA

Na-D2EHPA was prepared by converting the functional group of D2EHPA with sodium ion (Na^+). 40 mL of 0.75 M NaOH solution was shaken with 30 mL of D2EHPA (various concentrations) in an air bath shaker at 25°C and 200 rpm for 13 hours. After mixing the solution, pH increased sufficiently (~ 6), as NaOH is alkaline, and that is why, further increase of pH for preloading Na+ was not required, as it was done in the case of Co-D2EHPA. The organic was then separated and centrifuged to get Na-D2EHPA, which was later used as the extractant in the solvent extraction process. Table 3.2 shows the results of Cd extraction with various concentration of Na-D2EHPA, where it can be seen that cadmium extraction increases with the increase of extractant concentration.

Table 3.2 Results of Cd extraction with different concentration of Na-D2EHPA

[Feed: Cd = 55 ppm, A/O = 1]

Na-D2EHPA (vol.%)	Raffinate pH	Cd Conc. in Raffinate (ppm)	% Cd Extraction
5	6.04	42.23	23
10	5.99	35.94	34
15	6.25	30.93	43
20	6.51	25.05	54
25	6.61	24.18	56

The data presented in Table 3.2 was extracted from Appendix B5. In this experimental result, it was found that extraction of cadmium was achieved at higher pH (>6). In fact, during extraction of Cd, Na^+ ion from the extractant (Na-D2EHPA) is transferred into the aqueous solution through ion-exchange mechanism. As a result the pH of the aqueous solution goes high. Later, the extraction of Cd was investigated using Co-D2EHPA at different equilibrium pH, where pH of the solution was possible to control at desired level. Due to the transfer of Co^{2+} ions into the solution, pH was not drastically increased as it happened in the case of Na-D2EHPA and hence Co-D2EHPA was found suitable compared to Na-D2EHPA for the extraction of cadmium.

3.4.2 Preparation of Co-D2EHPA

Co-D2EHPA was prepared by pre-loading cobalt ion (Co^{2+}) into D2EHPA. This was done by mixing a 200 mL cobalt sulphate synthetic solution (prepared by dissolving $CoSO_4.7H_2O$ salt in de-ionized water) with 150 mL of D2EHPA (25 vol.%) in a magnetic stirrer. The equilibrium pH of the solution was varied from 3.0 - 6.7 to determine the maximum loading of cobalt in D2EHPA. The organic was then separated and centrifuged to get Co-D2EHPA. The results of cobalt preloading into D2EHPA were presented earlier at Table 2.4 in Chapter 2.

The converted extractant Co-D2EHPA was then used in the solvent extraction experiment for the extraction of cadmium from the cobalt electrolyte solution. The results of

extraction of cadmium and cobalt using the extractant 'Co-D2EHPA' are presented in Table 3.3.

Table 3.3 Results of Cd and Co extraction with 25 vol.% Co-D2EHPA

[Conc. of metals in feed electrolyte: Cd = 54.62 ppm (rounded up to 55 ppm), Co = 55668 ppm]

Raffinate pH	A/O Ratio	Cd conc. in raffinate (ppm)	Co conc. in raffinate (ppm)	% Cd Extraction	% Co Extraction
3.5	1	23.72	55390	56.87	0.50
3.8	1	25.17	55176	54.24	0.88
4.0	1	24.54	51515	55.38	7.46
4.9	1	21.91	48532	60.16	12.82
5.4	1	22.39	49877	59.29	10.40

The above data was extracted from the metal analysis (Cd and Co) raw data provided in Appendix B5. The concentrations of cobalt were high and hence they were rounded up, which will not have any significant effect on the result on cobalt extraction. Cadmium extraction (%) versus raffinate pH was plotted in Figure 3.2 where it was found that at pH 3.5 significant amount of cadmium was extracted with negligible co-extraction of cobalt. Increasing further pH will result small increase of cadmium extraction however, a significant amount of cobalt also would be co-extracted which was not desirable.

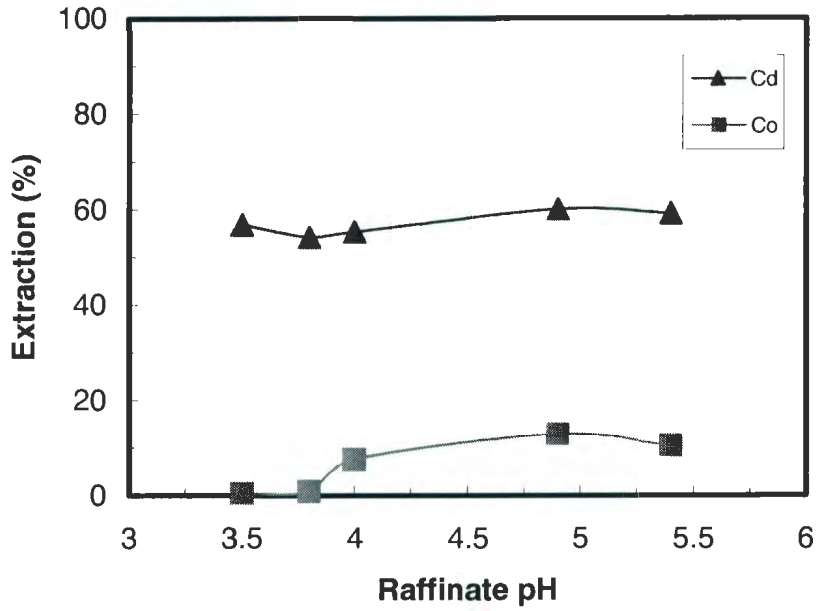

Figure 3.2 Cadmium and Cobalt extractions at different pH using 25 vol. % Co-D2EHPA

Figure 3.3 shows cadmium extraction at different pH using both Na-D2EHPA and Co-D2EHPA. It was found that Co-D2EHPA was suitable for a significant cadmium extraction at around pH 3.5. On the other hand, in the case of Na-D2EHPA, the extraction took place at higher pH (~ 6.5) as can be seen in Figure 3.3.

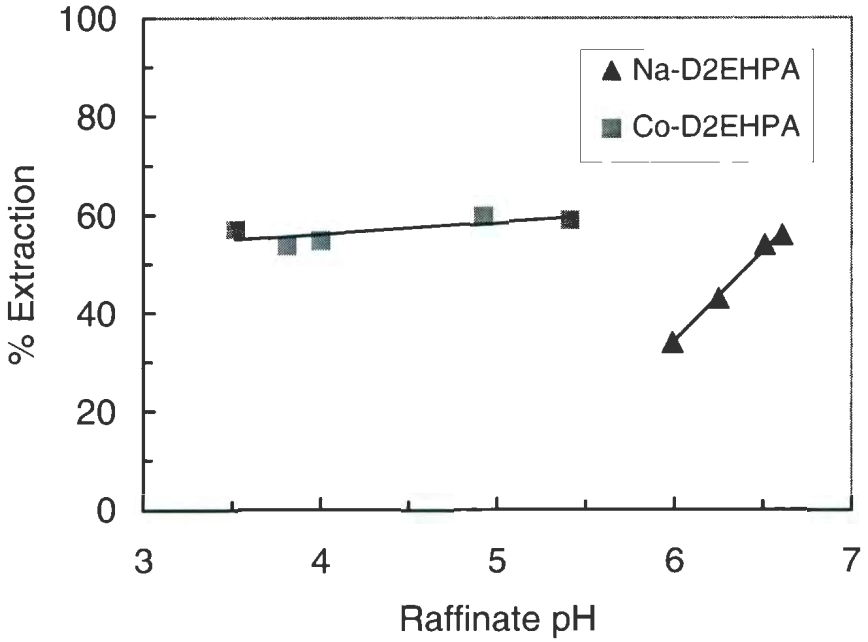

Figure 3.3 Cadmium extraction at different pH with 25 vol.% each of Na-D2EHPA and Co-D2EHPA

Kumar et al. (2009) also found similar extraction result for cadmium at around pH 3.5 using Na-D2EHPA. However, 100% cadmium was extracted in their study at pH around 6.0, which is not desirable in this study, because at pH 6.0 there will be a significant loss of cobalt through co-extraction.

3.4.3 Separation Factor of Cadmium and Cobalt

Separation factors were calculated from the distribution ratio of Cd and Co using equation 2.9, and tabulated in Table 3.4. Distribution ratio was defined in Chapter-2, which was calculated using equation 2.1. The raw data table is provided in Appendix B5.

Table 3.4 Effect of equilibrium pH on separation factors [Org. 25 vol.% D2EHPA in Escaid 110, O/A = 1, Temperature = 25 ^{o}C, $[Cd]_F$ = 55 ppm, $[Co]_F$ = 55668 ppm, $[pH]_F$ = 2.94, $D_{Cd} = [Cd]_O/[Cd]_A$, $\beta_{Cd\text{-}Co} = D_{Cd}/D_{Co}$]

Solution Item	pH				
	3.5	**3.8**	**4**	**4.9**	**5.4**
$[Cd]_A$ (ppm)	23.72	25.17	24.54	21.91	22.39
$[Cd]_O$ (ppm)	31.28	29.83	30.46	33.09	32.61
D_{Cd}	1.32	1.19	1.24	1.51	1.46
$[Co]_A$ (ppm)	55390	55176	51515	48532	49877
$[Co]_O$ (ppm)	278	492	4153	7136	5791
D_{Co}	0.005	0.009	0.081	0.147	0.116
$\beta_{Cd\text{-}Co}$	264.00	132.22	15.30	10.27	12.58

In the above table, subscript 'F' and 'A' stands for the aqueous feed and raffinate solutions, respectively. The data table is prepared from the data provided in Appendix B5. The effects of raffinate pH on the separation factors of Cd and Co is shown in Figure 3.4. As can be seen in the figure, the separation factor is high at pH 3.5 and this would be an important consideration for the selective extraction of cadmium over cobalt. Therefore, the choice of equilibrium pH is important for the extraction of metals of interest, as the extractions are pH dependent. A sample calculation for the distribution ratio and the separation factor of Cd and Co (at pH 3.5) is shown in Appendix C2.

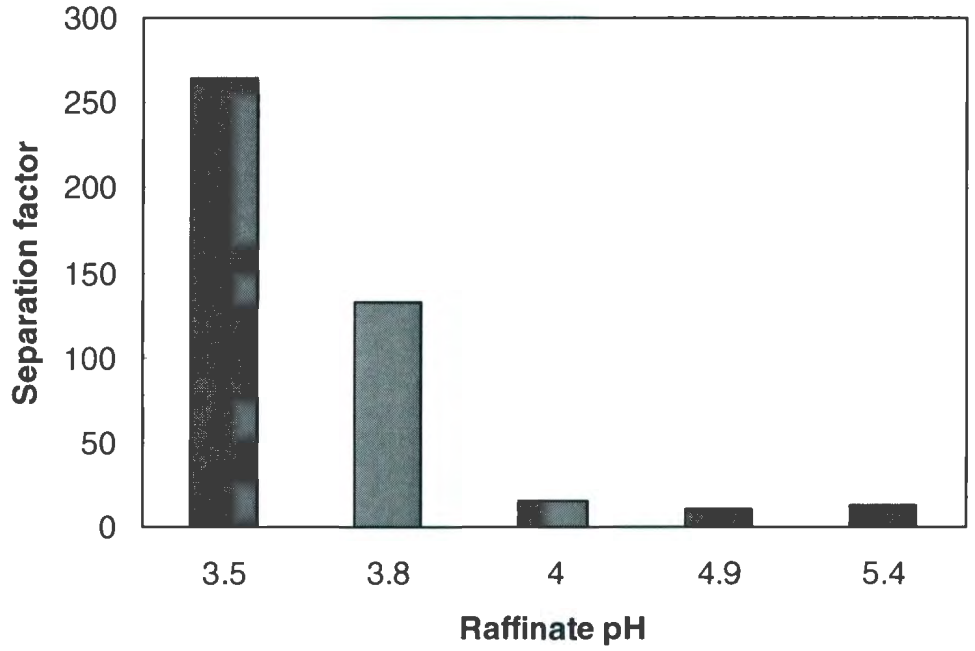

Figure 3.4 Effect of raffinate pH on separation factor for Cd and Co

3.4.4 Kinetics of Cadmium Extraction

The kinetic study for the extraction of cadmium was carried out using both of Na-D2EHPA and Co-D2EHPA. Table 3.5 shows the results for the extraction equilibrium of cadmium with 25 vol.% Na-D2EHPA. In this experiment, the concentration of Cd in the aqueous feed was 52.23 ppm and that of cobalt was 50335.08 ppm. The experiment was conducted at pH 5.5 with A/O = 1 and temperature of 25°C. The results are presented in Table 3.5.

Table 3.5 Results of kinetic Study for extraction of Cd and Co with 25 vol.% Na-D2EHPA

Time (min.)	Conc. of Cd in Raffinate	Conc. of Co in Raffinate	Cd extraction (%)	Cobalt extraction (%)
5	24.03	40260.15	53.99	20.01
10	20.90	38723.58	59.98	23.07
60	21.36	33343.19	59.10	33.76
120	21.14	34593.88	59.53	31.27
300	21.28	32891.55	59.25	34.65
600	22.85	35686.58	56.25	29.10

This data set corresponds to the 'Cd' and 'Co' column of metal analysis report provided in Appendix B6, (Sample: SK-1 ~ SK-6)]

The extraction (%) of Cd and Co with respect to time is plotted in Figure 3.5.a. It can be seen from the figure that the kinetics for the extraction of cadmium was faster than cobalt and equilibrium reached within a short time of contact of two phases. The faster kinetics and equilibrium of cadmium also can be clearly seen with better resolution of graph in Figure 3.5.b (log-log plot).

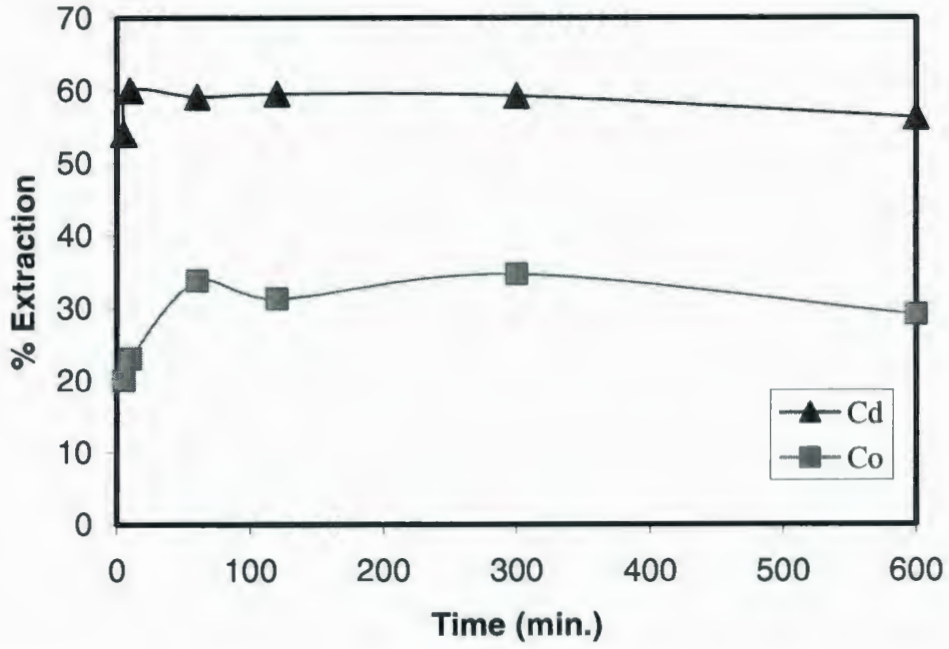

Figure 3.5.a Kinetics of cadmium and cobalt extraction with 25 vol.% Na-D2EHPA

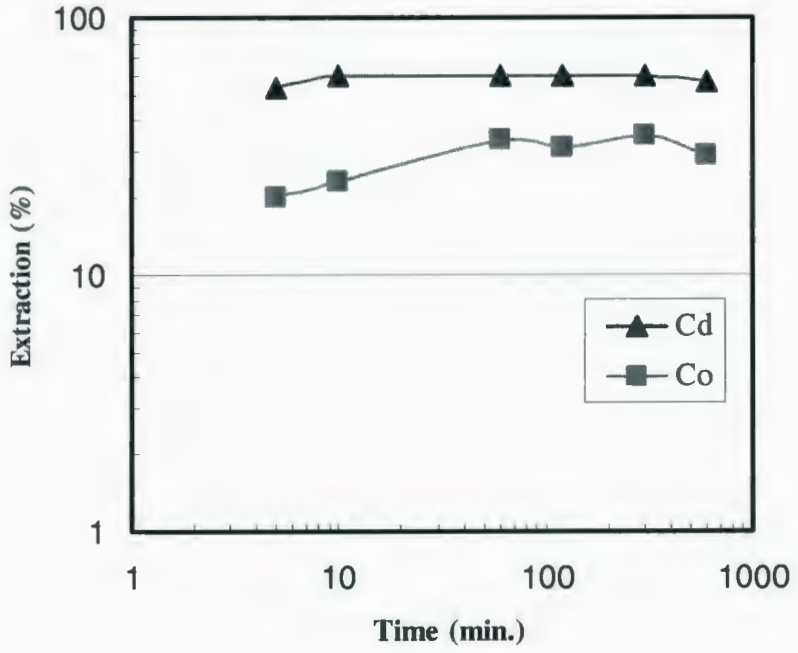

Figure 3.5.b Log-log plot showing kinetics of Cd and Co extraction with 25 vol. % Na-D2EHPA

The log-log plot (Figure 3.5.b) shows the results of kinetic studies for the extraction of metals (Cd and Co) with 25 vol.% Na-D2EHPA based on the data provided in Table 3.5. From this figure it is clear that the kinetics for cadmium extraction was very fast and equilibrium reached within 5~10 min. of contact time. However, the kinetics of cobalt extraction was not faster compared to that of cadmium. Kumar et al. (2009) also reported that cadmium extraction using D2EHPA was very rapid and equilibrium reached within a minute of contact time. From these experimental results, it can be concluded that based on the large difference of the extraction rate, the selective separation of cadmium over cobalt is also possible. The kinetic study of cadmium was also carried out using 25 vol. % Co-D2EHPA and the results are presented in Table 3.6.

Table 3.6 Results of kinetic study for extraction of Cd and Co with 25 vol.% Co-D2EHPA [Feed soln: Cd = 52.23ppm, Co = 50335.08 ppm, pH = 5.5, A/O = 1]

Time (min.)	**Conc. of Cd in raffinate (ppm)**	**Conc. of Co in raffinate (ppm)**	**Cd extraction (%)**	**Cobalt extraction (%)**
5	21.78	48553.57	58.30	3.54
10	20.2	49762.64	61.32	1.14
60	20.93	51105.94*	59.93	-
120	20.52	47578.13	60.71	5.48
300	20.34	49195.86	61.06	2.26
600	21.71	46612.78	58.43	7.40

*[*The concentration of Co in raffinate (51105.94 ppm) can not be higher than that of in the feed concentration (50335.08 ppm). Minimum extraction could be zero when there is no co-extraction of cobalt in the organic phase i.e. concentration of cobalt in the feed and raffinate should be equal, but this is also not realistic when the measurements are performed by any instrument*].

Figures 3.6.a shows the results of kinetic studies for the extraction of cadmium and cobalt with 25 vol.% Co-D2EHPA for the time span 0 - 600 minutes. It was found that the kinetics for the extraction of cadmium were very fast and equilibrium reached within a short time.

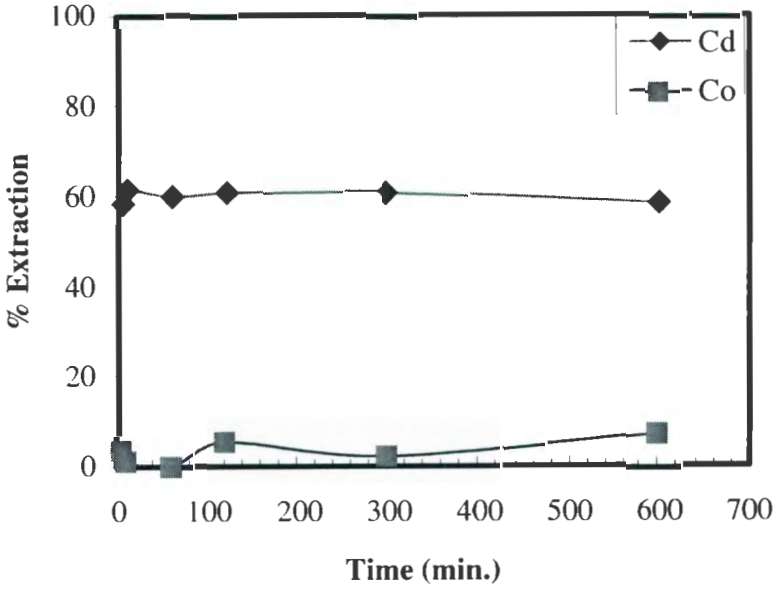

Figure 3.6.a Kinetics of Cd and Co extraction with 25 vol.% Co-D2EHPA

The results of kinetic study of cadmium extraction can be better understood with a log-log plot presented in Figure 3.6.b.

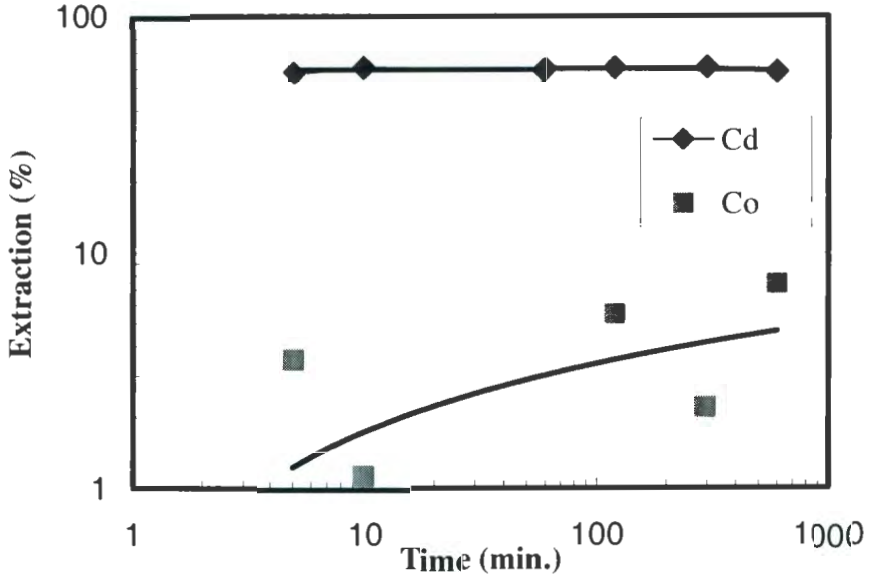

Figure 3.6.b Log-log plot showing kinetics of Cd and Co extraction with 25 vol. % Co-D2EHPA

As can be seen from the log-log plot (figure 3.6.b), the kinetics for the extraction of Cd was faster than that of Co and equilibrium reached within around 5 min. of contact time. The equilibrium of the extraction kinetics was also justified by the statistical estimates of relative standard deviation (RSD), obtained from the results of extraction versus time. The RSD for the concentrations of Cd for a time period 5 - 120 minutes was found 4.8%, and was 4.1% for throughout (0 – 600 min.) the time (Appendix D). From these statistical estimates, it can also be concluded that the concentration of Cd was not changed significantly after 5 min. and can be considered to have reached the equilibrium. On the other hand, the kinetics of cobalt extraction was slower and equilibrium could be achieved far later (as shown by the trend line). From the above experimental results it was observed that based on the difference of the kinetics of extraction, the selective

separation of cadmium over cobalt is possible allowing the above specified time (5 min.) for the extraction process.

3.4.5 Stripping of Cadmium

The stripping study for cadmium was also carried out using H_2SO_4 solutions. Literature searches revealed that dilute sulphuric acid performed well for the stripping of cadmium. Kumar et al. (2009) used sulphuric acid to strip the cadmium from loaded D2EHPA. Reddy et al. (2004) reported that 98% cadmium was stripped from loaded PC 88A using 0.1 M H_2SO_4.

In the present study, 0.02 M to 1.0 M H_2SO_4 were used to examine metal stripping from the loaded Co-D2EHPA. 20 mL of loaded organic and 20 mL H_2SO_4 were mixed and shaken in an air bath shaker with a shaking speed of 300 rpm and at 25°C for 2 hours. It was found that 100% cadmium was stripped at 0.4 M conc. of H_2SO_4 in a single stage. The pH of the raffinate solution was 1.4. Since sulphuric acid may also strip cobalt from the cobalt preloaded extractant, it is recommended that the stripping be carried out when organic is fully loaded with cadmium and other impurities. The results of stripping of cadmium are presented in Table 3.7.

Table 3.7 Stripping result of cadmium at different concentration of H_2SO_4

[Loaded org. feed: Cd* = 32 ppm, A/O = 1, Temp = 25 °C, Time = 2 Hrs.]

H_2SO_4 conc. (M)	**Cd conc. in stripping raffinate (ppm)**	**Sample no. in data sheet**	**Stripped Cadmium (%)**
0.02	<0.52	Str-1	ND
0.04	<0.52	Str-2	ND
0.06	0.77	Str-3	2.40
0.08	<0.60	Str-4	ND
0.10	0.87	Str-5	2.70
0.20	3.17	Str-6	9.90
0.40	35.26**	Str-7	100.00
0.50	39.18**	Str-8	100.00
0.80	39.16**	Str-9	100.00
1.0	37.34**	Str-10	100.00

Note: ND – Not Detected

[Cd = Conc. of cadmium in organic phase was obtained from the mass balance of Co-electrolyte (feed) and raffinate (denoted by CF-2 and SXR-2, respectively in the metal analysis data sheet provided in Appendix-B7.2).*

*** Concentration in the strip solution can not be greater than that of loaded organic (feed). Hence, it was considered that 100% metals were stripped.]*

Table 3.7 is prepared from the metal analysis raw data provided in Appendix B7.1 & B7.2. Figure 3.7 (semi-log plot) shows the stripping (%) of cadmium against the concentration (M) of H_2SO_4, where 100% Cd was stripped using 0.4 M H_2SO_4. It was

found that stripping starts to increase sharply at around 0.3 M H_2SO_4, and reaches to 100% with 0.4 M H_2SO_4.

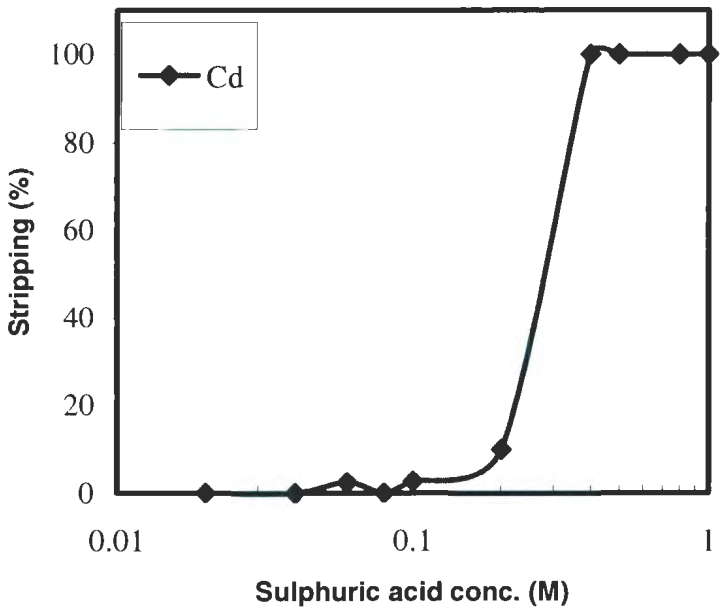

Figure 3.7 Stripping of cadmium at different concentration of H_2SO_4

3.4.6 Extraction Mechanism

In cobalt electrolyte solution, cadmium stays as divalent cationic species as Cd^{2+}. The organic extractant, di-2-ethyl-hexyl phosphoric acid (D2EHPA) is good for extracting cationic species from the aqueous solution, where hydrogen ions in the extractant are replaced with the metal ions as shown in Equation 3.1. Here, M^{n+} denotes the metal ion, RH is the extractant, and subscripts "org" and "aq" are the organic and aqueous phases, respectively.

$$[M^{n+}]_{aq} + n[RH]_{org} \longrightarrow [MR_n]_{org} + n[H^+]_{aq} \quad \text{.....(3.1)}$$

Na-D2EHPA

Preloading: $[NaOH]_{aq} + [RH]_{org} \longrightarrow [RNa]_{org} + [H_2O]_{aq}$ ..... (3.2)

Extraction: $[CdSO_4]_{aq} + 2[RNa]_{org} \longrightarrow [R_2Cd]_{org} + [Na_2SO_4]_{aq}$ .....(3.3)

Co-D2EHPA

Preloading: $[CoSO_4]_{aq} + 2[RH]_{org} \longrightarrow [R_2Co]_{org} + [H_2SO_4]_{aq}$ .....(3.4)

Extraction: $[CdSO_4]_{aq} + [R_2Co]_{org} \longrightarrow [R_2Cd]_{org} + [CoSO_4]_{aq}$ .....(3.5)

Equations 3.2 – 3.5 show the process reactions in the case of Na-D2EHPA and Co-D2EHPA, where Na^+ and Co^{2+} ions are preloaded into D2EHPA to convert its functional group (Equations 3.2 and 3.4, respectively). Divalent cadmium is extracted by converted extractant via a cation-exchange mechanism as shown in Equations 3.3 and 3.5.

3.5 Conclusion

A solvent extraction method has been examined to remove the cadmium impurity from a cobalt electrolyte solution containing large amount of cobalt, using modified D2EHPA. The functional group of D2EHPA was converted to form Na-D2EHPA and Co-D2EHPA by introducing Na^+ and Co^{2+} ions, respectively. Application of Co-D2EHPA for removal

of cadmium from the cobalt electrolyte solution is new and it has several advantages as mentioned earlier. Experimental results revealed that Co-D2EHPA was superior to Na-D2EHPA, where about 60% cadmium was selectively removed from the cobalt electrolyte solution by 25 vol.% Co-D2EHPA at an equilibrium pH of around 3.5, without losing any cobalt through co-extraction. When pH went over 5, extraction of cadmium was high, but a certain amount of cobalt was also co-extracted which was not desirable. Kinetic of cadmium extraction was very fast and equilibrium was attained within 5 ~ 10 minutes in the case of Na-D2EHPA and 5 minutes in the case of Co-D2EHPA. Stripping result of cadmium from the loaded organic showed that 100% cadmium can be stripped using 0.4 M H_2SO_4 with O/A ratio 1.

CHAPTER 4

Removal of Manganese and Cadmium from Cobalt Electrolyte Solution by Ion Exchange / Adsorption Method

4.1 Introduction

Ion exchange method is more efficient to remove the trace amount of target metals from a solution, and that is why, ion exchange method is also introduced in this study. In fact, ion exchange screening tests were only carried out in this study due to the limited time constraint in the program. Ion exchange resins with different functional groups, which are commercially available, were tested in screening tests to selectively remove manganese and cadmium from the cobalt electrolyte solution. The ion exchange resins were selected depending on the cationic impurity species (manganese and cadmium) in the cobalt electrolyte solution. A significant amount of manganese and cadmium impurities was extracted using resins Amberjet 4400 Cl, Amberlite IRC 748I and Lewatit TP-207.

4.2 Experimental

4.2.1 Reagents

i. Ion exchange resins with different functional group (as listed in Table 4.1)

ii. Real plant solution (cobalt electrolyte solution)

Screening test with different resins was carried out batch wise, where 0.50 g of the exchangers and 20 mL of aqueous feed solution were shaken in an air bath shaker with the controlled environment at 25°C with a shaking speed of 200 rpm over the period of 6 hours to attain equilibrium. After shaking, aqueous solution was separated from the exchanger by filtration. Initial and equilibrium concentrations of metal ions in the aqueous solutions were determined by ICP-MS. The amount of adsorbed/exchanged metal ion in the resin was calculated from the difference in metal concentration of aqueous feed and raffinate solution.

4.3 Adsorption mechanism

In ion exchange method, there is an interchange of ions between two phases. Exchange of ions with the same charge occurs in ion exchange with resins contacted into the solution containing the desired metal ions (Alexandratos, 2004). The author showed the mechanisms of ions as given below:

For anion exchange resin:

$$[R] - X^+ A^- + B^- \longrightarrow [R] - X^+ B^- + A^- \quad \text{.....(4.1)}$$

For cation exchange resin:

$$[R] - Y^- C^+ + D^+ \longrightarrow [R] - Y^- D^+ + C^+ \quad \text{.....(4.2)}$$

Where, [R] indicates polymer and X, Y are functional group. A, B, C, and D are exchangeable ions.

4.4 Results and Discussion

In this experiment different ion exchange resins as listed in Table 4.1 were tested by a batch adsorption test to find the most suitable exchanger for the selective separation of Mn and Cd from cobalt electrolyte solution.

In this experiment, 0.5 g resin of each was added to 20 mL of cobalt electrolyte solution and stirred at about 200 rpm and at 25°C in an air bath shaker (model: Innova-43 from New Brunswick Scientific) for a period of 1 hour. The pH of the feed solution was 2.95, concentration of Mn and Cd was 742 and 55 ppm, respectively (Appendix B1). Concentration of cobalt in the feed solution was about 42 g/L. The results of extraction of Mn and Cd are tabulated in Table 4.1.

Table 4.1 Adsorption (%) of manganese and cadmium by IX resin

Item no.	Resin	Mn Conc. in Feed ppm	Cd Conc. in Feed ppm	Mn conc. in Raffinate ppm	Cd Conc. in Raffinate ppm	Mn Adsorption (%)	Cd Adsorption (%)
1	Lewatit TP - 207	742	55	676	52	8.9	5.5
2	Dowex G -26	742	55	710	53	4.3	3.6
3	Dowex Mac- 3	742	55	711	53	4.2	3.6
4	Dowex 21kXLT	742	55	750*	47	-	14.5
5	Amberlite IRC 748I	742	55	669	46	9.8	16.4
6	Amberjet 4400 Cl	742	55	662	34	10.8	38.2

* *Error: The concentration of Mn at raffinate can not be higher than that of in feed solution.*

Table 4.1 is prepared from the metal analysis raw data table provided in Appendix B2 (Sample # R1 ~ R4), and Appendix B3 (Sample R5 ~ R6), which refers to the item no.1 through 6 in the above table. Some data values were rounded up to the nearest value as they have no significant effect on the results. The concentrations of metals in the aqueous feed and raffinate (equilibrium) solution were measured by ICP-MS and the percent metal adsorbed by the resin was obtained from the mass balance.

The results are also presented in a graphical presentation (Figure 4.1) for a quick overview of the adsorption status of metals using different IX resins.

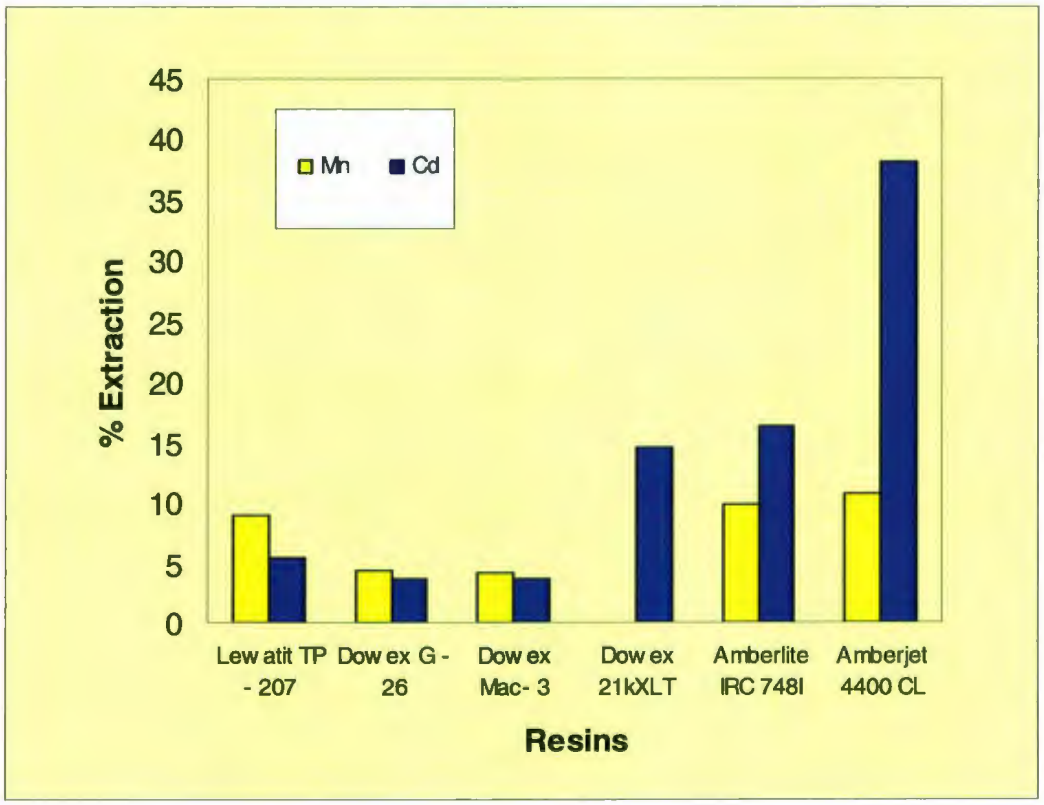

Figure 4.1 Mn and Cd adsorption with different ion-exchange resin

As can be seen from the above graph that Amberjet 4400 Cl has the highest affinity for adsorption of 38% Cd and 11% Mn, followed by Amberlite IRC 748I and Lewatit TP-

207. It is worth mentioning here that there was no co-extraction of cobalt found in this experiment. The physical and chemical properties of above three useful ion exchange resins for these experiments are given in Table A.5, A.6 and A.7 at Appendix - A.

4.5 Recommendation Regarding Treatment of Resins

The IX resins used in this experiment were as received condition i.e. they were not treated or washed further in the laboratory. As the resins may contain some impurities, therefore, using the selected resin after proper conditioning e.g. washing by acid or base, rinsing and drying, may give better result.

It can be further mentioned here that due to the limited selectivity of the cationic ion-exchange resin, chelating resin is also useful to get the higher selectivity for particular metal ions of interest.

4.6 Conclusion

Screening tests for the ion exchange / adsorption of manganese and cadmium from sulphate media were carried out with some commercial cation exchange and chelating resins. It was found that Amberjet 4400 Cl has the highest affinity with adsorption of 38% Mn and 11% Cd followed by Amberlite IRC 748I and Lewatit TP-207. After proper conditioning of these resins and using those in ion exchange process will give significant

results in this field. The experiments on ion exchange with selective resins varying the process parameters, such as pH, time, temperature and concentration were not done due to the limited time constraint of this study.

CHAPTER 5

Discussion and Conclusion

5.1 Discussion

5.1.1 Losses of Solvent in the Solvent Extraction Process

In solvent extraction process, losses of solvents are major concerns. It is obvious that ion exchange method is convenient for extraction of trace amounts of metals from aqueous solutions keeping the environment clean and healthy, however, engineering or industrial research and development on ion-exchange at a large scale has not yet been developed. On the contrary, precipitation methods create process burden as well as disposes more waste to the environment. That is why, solvent extraction method would be a suitable method in the metallurgical industries considering the balance of the plant output and environmental aspect. It is worth mentioning here that in solvent extraction process, solvent losses issue is significant considering the process efficiency, plant output and environmental aspects. The advantages of solvent extraction process can not be achieved if the loss of solvent in the process is high. It is not possible to eliminate the losses of solvents totally, however, there should be efforts to minimize the losses. The losses of solvents in the solvent extraction process include solubility of solvent in the aqueous phase, entrainment, evaporation or volatization, degradation and crud formation (Rydberg et al., 1992). For many systems, the two phases (aqueous and organic) are considered totally immiscible. But in some cases, there may be some miscibility for which solvent is

lost. Consideration of proper phase ratio (A/O) during solvent extraction process is an important parameter among some others to minimize the losses of solvents. For example, high aqueous/organic (A/O) ratio may lead to high solvent losses. On the other hand, high organic/aqueous (O/A) ratio may lead to the increased consumption of organics in the process, resulting in higher inventory costs. Losses of solvents may also occur due to misting or aerosol formation, as well as during sampling or spilling from the equipment. Although losses of solvents due to the solubility in the aqueous phase are less, entrainment losses occur considerably which can be overcome with good equipment design and proper selection of diluents (Rydberg et al., 1992). The operating temperature and the enclosure of the system is also an important consideration to minimize the evaporation loss of solvent (Rydberg et al., 1992). Crud is another reason for solvent losses in the solvent extraction process, which is occurred in the presence of suspended solids and emulsification of aqueous and organic phases that becomes stable. Rydberg et al. (1992) mentioned some factors, such as reagent choice, nature of feed, equipment selection and method of operation (e.g. droplet size continuous phase, excessive turbulence) that may play an important role for the formation of crud.

Degradation of extractant in the solvent extraction process is a major concern. The degradation of solvent can arise from various sources, such as elevated temperature, high acidity, sunlight, and bacteria (Ritcey, 2006). To minimize the degradation of extractant it is important to select an extractant with low solubility, high stability and having resistance to oxidation. However, the extractant should have good solubility to the diluents so that required physio-chemical properties can be achieved. Rydberg et al. (1992) reported that the degradation of an extractant is a function of the stability of the

extractant, composition of the aqueous phase, and temperature. The author also added that the solubility of extractant can be increased due to the dominating parameters in the system, such as pH and salt concentration of the aqueous phase in some cases. Bautisca (1993) carried out some case studies including the cobalt /nickel separation from the acid solution using D2EHPA, and reported that the solubility of D2EHPA was 30 ppm at an equilibrium pH of 6.0, which was found from the analysis of the raffinate from a pilot plant study. Ritcey (2006) found that the change of oxidation state of manganese to permanganate in some copper circuits caused reagent degradation when permitted to enter into the electrowinning (EW) circuit, however, it was also mentioned that if there was sufficient Fe/Mn ratio (10/1), the effect was minimized. Based on the test carried out in a mini-pilot plant, the authors also reported that that Cyanex 301 degrades faster (8 days) than Cyanex 302 (40 days) by oxidizing to the disulphides. It was found in another study (Parker Centre, 2002/2003) that the increase in temperature and presence of an oxidant contribute to organic degradation for the extractant Cyanex 272. Cheng et al. (2000) observed during copper SX-EW trials that due to the oxidation state of manganese to the higher state, oxidation of solvent during extraction and stripping stage was happened, which created other problems in the process, such as poor phase separation and stable emulsion formation.

5.1.2 Consequences of Organic Losses

The following consequences will be there due to the losses of organics during solvent extraction process:

1) Since the organic solvents are expensive, the replacement or making up the losses of organics increases the operating cost of a plant. Capital investment is also involved when the additional engineering cost for the sizing of equipment or the process such as scrubbing is required.

2) Cost of regeneration and/or pH maintenance facilities need to be included into the system. The efficiency of plant also goes down due to the poor extraction and stripping.

3) Problems arise in the electrowinning cell when organics are oxidized or enter into the EW cell with the aqueous phase.

4) Difficulties with the phase separation and emulsion formation after solvent extraction and stripping stages.

5.1.3 Minimization of Organic Losses

The losses of organics may be minimized if attentions are paid on the followings:

1) Proper choice of process parameters (temperature, pH, concentrations, nature of solvents and phase continuity).

2) Consideration of physical and chemical properties of organic should be taken carefully before selection and use.

3) Appropriate plant and process design, and engineering can minimize the solvent losses by avoiding mist and aerosol formation.

4) During SX process additional settling time should be allowed to settle the entrained organic out of the aqueous phase. Efficient equipment also should be introduced to obtain better separation. Introduction of appropriate filtration system may help.

5) The organic should be treated through a regeneration or crud-treatment process before it is returned to the SX circuit. Washing of solvents also may be done using proper diluents.

5.2 Conclusion

5.2.1 Research Conclusion

The focus of this research was to mitigate the practical challenges associated with the cobalt electrolyte solution purification in the mining and metallurgical industry. Within the research time frame, several literature reviews have been done on the existing technology of solvent extraction and ion exchange processes related to solution purification, especially removal of manganese and cadmium impurities from the cobalt electrolyte solution by solvent extraction method. Generally, a precipitation method is adopted in the industries to remove the impurities, which is neither cost effective nor easy to control the operations. In order to overcome such challenges, solvent extraction method was studied and elaborated. Ion exchange method was also considered in this research by carrying out number of limited experiments. The suitable resins for the

adsorption of Mn and Cd were found. All the aspects of ion exchange technology and the ion exchangers were not studied in this research, however, the screening test results found in this study will benefit in future research.

In the solvent extraction method, significant amounts of manganese and cadmium were selectively removed from the cobalt electrolyte solution using the modified extractant (Co-D2EHPA) which is new in this field. From the screening test by ion exchange method, it was found that Mn and Cd can be removed from the cobalt electrolyte solution using Amberjet 4400 Cl , Amberlite 748I resin and Lewatit TP-207.

5.2.2 Significance and Accomplishment of this Work

This proposed work is important for the optimization of the important process parameters used for the recovery of pure cobalt, as well as minimization of impurities in the process circuit. Solvent extraction method is much favorable compared to that of precipitation method. Ion-exchange is an efficient and easy technique to remove trace amounts of elements from process stream in a cleaner way and offers benefits over traditional precipitation practice. The process studied in this work is efficient, cost effective, and sustainable, which may have significant benefit for the mining industries. Hydrometallurgy lab at Memorial University has been installed and set up recently and this is the first research in this lab. Therefore, this work will give an opportunity to other graduate or undergraduate students to continue to develop knowledge and skills in the hydrometallurgical processes.

Accomplishment

A portion of this thesis has been published in the Proceedings of the International Symposium, 39th Annual Hydrometallurgical Meeting Held in Conjunction with Nickel and Cobalt 2009, Sudbury, Ontario, Canada (Hossain et al., 2009).

5.2.3 Future Work and Suggestions

For implication of this research in the industry level some other experiments need to be done to fulfill the requirements, such as:

(a) For solvent extraction method,

I. Theoretical stages for extraction needs to be determined using counter current extraction process.

II. Determination of metal-organic complex species.

III. The solvent extraction of Mn and Cd may be carried out with different A/O ratio and McCabe-Thiele diagram may be constructed for finding the number of stages in the extraction, as well as in the stripping process. The optimization (using computer software, such as Design Expert 7.1.3) for a pH value and other parameters such as temperature, organic and aqueous concentration, etc. may give promising result in this regard which was not conducted in this study due to the limited time constraint.

IV. Study on the stripped organic and associated losses of solvent needs to be carried out to reuse the extractant efficiently for several cycles in the

process. Determination of solvent degradation is also important in this case for minimizing the inventory cost.

V. A process flow sheet can be designed for the purification stage, based on the results obtained from the extraction and stripping of Mn and Cd from the cobalt electrolyte solution.

(b) For ion exchange method,

The study may be continued for optimization of the process parameters as discussed in the respective chapter using the selective resins from the screening test.

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APPENDIX A

Table A.1: Physical and chemical properties of cobalt electrolyte solution

(source: MSDS supplied by the manufacturer)

Parameter	**Information**
Product Identifier	Cobalt strip product
Synonyms	Cobalt electrowinning feed
Manufacturer	Vale Inco Newfoundland & Labrador Ltd, Argentia, NL, Canada
CAS #	10124 – 43 – 3
Physical state	Liquid
Appearance and Odour	Clear, purple, odourless solution
Boiling point/Boiling Range	Similar to water
Freezing point	Similar to water
Vapour Pressure	Similar to water
Density	1.3 g/mL
Specific Gravity (H_2O = 1)	1.3
Conditions of flammability	Not flammable
Stability	Stable at temperatures from 0 – 100°C

Appendix A contd.

Table A.2: Physical and chemical properties of D2EHPA (MSDS: www.alfa.com)

Parameter	Information
F.W.	322.42
Form	Liquid
Color	Colorless
Odor	Not determined
Melting point/Melting Range	Not determined
Boiling point/Boiling Range	Not determined
Flash point	> 110°C (>230°F)
Density	0.965 g/cm^3

Appendix A contd.

Table A.3: Physical and chemical properties of 1-Decanol (MSDS: www.alfa.com)

Parameter	**Information**
Form	Viscous Liquid
Color	Colorless
Odor	Sweet
Melting point/Melting Range	7°C (45°F)
Boiling point/Boiling Range	229°C (444°F)
Flash point	82°C (180°F)
Density	0.8287 g/cm^3

Appendix A contd.

Table A.4: Physical and chemical properties of cobalt sulphate heptahydrate ($CoSO_4.7H_2O$) (MSDS: www.alfa.com)

Parameter	Information
CAS #	10026 – 24 - 11
Form	Crystalline
Color	Violet
Odor	Odorless
Melting point/Melting Range	96.8°C (206°F)
Boiling point/Boiling Range	Not determined
Danger of explosion	Product does not present an explosion hazard
Flash point	Not applicable
Density at 20°C (68°F)	2.03 g/cm^3
Solubility in/Miscibility with water at 3°C (37°F)	604 g/L

Appendix A contd.

Table A.5: Typical /Physical and Chemical Properties of Amberjet 4400 CL (ROHM & HAAS)

[Source: http://www.rohmhaas.com/wcm/products/product_detail.page?display-mode=msds&product=1123226]

Table A.5.1 Product Data Sheet Amberjet 4400 CL

Physical form	Light amber spherical beads
Matrix	Styrene divinylbenzene copolymer
Functional group	Trimethyl ammonium ($C_3H_{10}N$)
Ionic form as shipped	Cl^-
Total exchange capacity [1]	≥ 1.40 eq/L (Cl- form)
Moisture holding capacity [1]	40 to 48 % (Cl- form)
Shipping weight	730 g/L
Particle size	
Uniformity coefficient [1]	≤ 1.2
Harmonic mean size	0.53 – 0.63 mm
< 0.425 mm [1]	0.5 % max
Maximum reversible swelling	Cl- → OH- < 30 %

[1]

Contractual value

Test methods available upon request

Appendix A contd.

Table A.5.2 Suggested Operating Conditions of Amberjet 4400 CL (Water Treatment)

Maximum operating temperature	60°C
Minimum bed depth	800 mm
Service flow rate	5 - 50 BV*/h for make-up water 30 - 120 BV/h for condensate polishing
Maximum service velocity	60 m/h for make-up water 120 m/h for condensate polishing
Regeneration	
Regenerant	NaOH
Level	40 to 100 g/L 80 to 200 g/L for condensate polishing
Concentration	2 to 5 % NaOH
Minimum contact time	20 minutes
Slow rinse	2 BV at regeneration flow rate
Fast rinse	3 to 6 BV at service flow rate

1 BV (Bed Volume) = 1 m3 solution per m3 resin

Appendix A contd.

Table A.5.3: Physical and chemical properties of Amberjet 4400 CL

Form	Beads
Colour	white /opaque
Odour	amines
Boiling point/range	100°C (212.00°F) Water
Melting point/range	0°C (32°F) Water
Flash point	not applicable
Ignition temperature	>500°C (932.00°F)
Lower explosion limit	not applicable
Upper explosion limit	not applicable
Vapour pressure	17.0 mmHg at 20°C (68.00°F) Water
Relative vapour density	<1.0water
Water solubility	practically insoluble
Relative density	1.07
Viscosity, dynamic	not applicable
Evaporation rate	<1.00 Water
Percent volatility	50 - 56 %

NOTE: The physical data presented above are typical values and should not be construed as a specification

Appendix A contd.

Table A.6: Typical / physical and chemical properties of Amberlite IRC 748 (Rohm & Haas)

[Source: http://www.rohmhaas.com/wcm/products/product_detail.page?display-mode=msds&product=1120260]

Table A.6.1: Typical Properties

These properties are typical but do not constitute specifications.	
Matrix	Macroporous styrene divinylbenzene
Functional groups	Iminodiacetic acid
Physical form	Opaque, beige beads
Ionic form as shipped	Na^+
Total exchange capacity [1]	$\geq$ 1.35 eq/L (Na^+ form)
Moisture holding capacity [1]	60.0 to 65.0 % (Na^+ form)
Shipping weight	750 g/L (46.8 lb/ft^3)
Particle size	
Harmonic mean size [1]	0.50 - 0.65 mm
Uniformity coefficient	$\leq$ 1.7
Fine contents [1]	< 0.300 mm : 1.0 % max
Coarse beads	> 1.100 mm : 5.0 % max
Typical reversible swelling	H^+ ® Na^+ : 30 %
[1] Contractual value Test methods available upon request	

Appendix A contd.

Table A.6.2: Physical and chemical properties of Amberlite IRC 748

Form	Beads
Colour	amber
pH	8.0 - 9.0Aqueous slurry
Boiling point/range	100°C (212.00°F) Water
Ignition temperature	> 500°C (> 932.00°F) estimated
Lower explosion limit	Not Applicable
Upper explosion limit	Not Applicable
Vapour pressure	17.0 mmHg at 20°C (68.00°F) Water
Relative vapour density	<1.0 water
Water solubility	practically insoluble
Relative density	1.14
Viscosity, dynamic	Not Applicable
Viscosity, dynamic	Not Applicable
Evaporation rate	<1.00 Water
Percent volatility	60 - 65 %

NOTE: The physical data presented above are typical values and should not be construed as a specification

Appendix A contd.

Table A.7: Physical and chemical properties of Lewatit Monoplus TP-20795900-B)

Appearance/Parameters	**Name of the supplier**
Product name	Lewatit Monoplus TP – 207 95900-B)
Company	Sybron chemicals, Inc; LANXESS Corporation, USA
Form	Solid
Appearance	Beads
Color	Beige, Opaque
Odor	Odorless
pH	Approximately 9, aqueous suspension
Melting point	> 200°C (>392°F)
Boiling point/Range	Not Established
Flash point	Not Established
Sp. Gravity	Approximately 1.17
Solubility in water	Not applicable
Autoignition Temperature	> 300°C (572°F)
Bulk Density	700 – 800 kg/m^3
Supplier	Sybron Chemicals Inc., LANXESS Corp., USA

APPENDIX B

APPENDIX B1.0 (Metal concentrations in Co-electrolyte)

file =	0										
run =	waters										
owner =	AlamHossain										
date =	Jan 21 09 11:18 am										
calculated:	21-Jan-09	13:47:21									
waters (w), biol. (b):	w										
avg diln g/g:	0.01837										
conc given in:	ppb										
conc in:	wet										
interference correction?						Ca	Ca	Ca			
intf. factor						8484	50113	-10329			
ppm intf.						4	4	4			
lld - intf.						13.316	3.342	1.124			
lld - ppb/ppm						1.681	0.4462	0			
lld - blank	5.511	3.859	22.657	98.98	0.215	6.52	1.538	78.314	1.015	2.422	
bk average											
Sample	**Li 7**	**Be**	**B**	**Fe 54**	**Mn**	**Co**	**Ni**	**Cu**	**Cd**	**Sn**	**Sample**
name	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	diln g/g
blanknano-1	<9.77	<6.84	<40.16	<175	<0.38	<11.33	<2.67	<138.82	<1.80	<4.29	0.010364
Alam	<543.76	<380.70	67204.56	10246	741634.1	42796084	78833.88	<7726.61	54777.26	<238.92	0.000186
Alamdup	<501.72	360.61	63690.85	<9011	719650.81	41643736	75702.01	<7129.17	54060.39	<220.44	0.000202

APPENDIX B1.1 (Extraction of Metals with D2EHPA)

file =			0												
run =			waters												
owner =			Hossain(Alam)												
date =			Feb 03 09 11:26 am												
calculated:			04-Feb-09	11:25:26											
waters (w), biol. (b):			w												
avg diln g/g:			0.030256												
conc given in:			ppm												
conc in:			wet												
interference correction?								Ca	Ca	Ca	Ca	Ca			
intf. factor								515	326	5780	35057	13470			
ppm intf.								4	4	4	4	4			
lld - intf.								1.473	0.132	0.01	0.001	0.001			
lld - ppb/ppm								0	0	0.0021	0	0			
lld - blank		0.005	0.001	0	0.041	3.759	0	6.314	1.505	0.002	0.002	0.028	0.001	0.001	
bk average															
Sample		**Li 6**	**Li 7**	**Be**	**B**	**Fe 54**	**Mn**	**Fe 56**	**Fe 57**	**Co**	**Ni**	**Cu**	**Cd**	**Sn**	**Sample**
name		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	diln g/g
blank-nano-1		0	0	0	<0.01	<1	<0.00	<2	0	<0.00	0	<0.01	<0.00	<0.00	0.10077
t171		0.01	0.01	0	0.02	<1	0.01	<2	<0	0	0.01	<0.01	0	0	0.10563
t153		0.06	0.05	0	0.09	<1	0.07	<2	0	<0.00	0.03	0.06	0.02	0	0.10271
m31851u	MH 5%	<0.02	0	0.02	0.6	<11	6.76	<19	<5	416	0.78	<0.08	0.51	<0.00	0.01011
m31852n	MH 10%	3.04	1.44	0.46	61.31	<917	634.02	<1541	72	41070	75.77	3.12	48.26	<0.19	0.00012
m31853g	MH 20%	4.26	0.46	0.9	63.77	<863	563.48	<1450	80	41336	76.93	11.91	45.63	0.43	0.00013
m31853gdup		3.04	0.34	0.91	64.29	<1003	588.93	<1684	126	43267	78.47	8.49	47.56	<0.21	0.00011

APPENDIX B2 (Results of screenig tests with extractant and resins)

file =		0												
run =		waters												
owner =		LCave/MHossain												
date =		Feb 23 09 11:51 pm												
calculated:		23-Feb-09	15:48:33											
waters (w), biol. (b):		w												
avg diln g/g:		0.036511												
conc given in:		ppm												
conc in:		wet												
interference correction?													Cl	
intf. factor													40899	
ppm intf.													25	
lld - intf.													0.04	
lld - ppb/ppm													0.0006	
lld - blank		0.003	0.02	0.024	0.032	0.173	1.126	0.86	39.047	15.175	5.546	0.106	0.024	0.003
bk average														
Sample		**Li 7**	**Be**	**B**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ca 43**	**Ti**	**V**	**Cr 52**
name		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
blanknano-1		<0.00	<0.01	<0.01	<0.0	<0.1	<0	<0	<14	<5	<2	0	<0.01	<0.00
t171		0.01	<0.01	0.03	3	<0.1	2	0	<14	11	6	0	<0.01	0
t143		0.02	0.01	0.04	10	<0.1	10	0	<13	23	53	0	0.03	0.04
t145		0.02	<0.01	0.04	8	<0.1	5	<0	<14	39	30	-0.01	0.01	0.01
t155		0.03	<0.01	0.1	12	<0.1	5	<0	25	23	43	-0.01	0.02	0.01
t153		0.05	<0.01	0.1	9	<0.1	2	<0	15	33	27	-0.01	0.01	0.01
blank-nano-2		<0.00	<0.01	<0.01	0	<0.1	<0	<0	<14	49	3	<0.04	0.13	0.01
m31888z	**S-1**	<0.76	<5.88	39.15	7969	<50.9	<331	<253	68904	16954	<1631	6.07	61.45	2.33
m31889a	**S-2**	<0.87	<6.68	54.82	8170	<57.9	20	<288	70686	10631	<1855	<35.55	32.99	<1.16
m31890t	**S-3**	<0.83	<6.41	49.2	7864	<55.5	<361	<276	65664	5365	109	<34.09	19.82	<1.11
m31891x	**S-4**	<0.76	<5.90	50.73	7847	<51.1	<332	<254	73232	<4478	416	<31.37	13.83	0.12
m31892b	**S-5**	<0.86	<6.63	49.17	7761.9	<57.4	<374	<285	72687	<5037	<1841	<35.29	10.69	0.09
m31893f	**S-6**	<0.79	<6.10	64.42	8079	<52.8	<344	<262	69000	<4632	<1693	1.89	<7.26	<1.06
m31894k	**S-7**	0.85	<5.58	70.11	8144.8	<48.3	43	<240	73154	2903	<1549	2.29	<6.72	<0.97
m31895o	**S-8**	<0.77	<5.97	58.65	8034.8	<51.7	<337	<257	72065	<4534	<1657	8.6	<7.11	<1.03
m31896s	**R-1**	<0.69	<5.34	60.36	7644.7	<46.3	<301	<230	69627	<4055	<1482	0.93	<6.36	<0.92
m31897w	**R-2**	<0.75	<5.79	60.02	7957	<50.1	<326	35	75706	<4397	<1607	7.58	<6.91	<1.00
m31898a	**R-3**	<0.73	<5.66	67.51	8004.3	<49.0	<319	<244	75931	<4299	<1571	<30.12	<6.76	<0.98
m31899e	**R-4**	<0.72	<5.58	73.8	8493.3	<48.3	<314	48	80932	<4234	<1547	<29.67	<6.69	<0.97

APPENDIX B2 (Results of screenig tests with extractant and resins)

			Ca	Ca	Ca	Ca		Cl		Br					
			410	4769	59893	12253		183862		3217					
			4	4	4	4		25		0					
			0.561	0.036	0.002	0.007		0.005		0.044					
			0.0549	0.0063	0	0		0.0001		0					
		0.001	0.339	0.011	0.003	0.007	0.022	0.003	0.042	0.107	0	0.002	0.001	0	0.001
Sample		**Mn**	**Fe 57**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Br**	**Se**	**Rb**	**Sr**	**Mo**	**Ag**	**Cd**
name		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
blanknano-1		0	<0	<0.00	0.01	0.02	0.03	0	<0.01	<0.04	0	<0.00	<0.00	<0.00	<0.00
t171		0.01	<0	<0.01	0.01	<0.00	0.01	0	<0.01	<0.04	0	0.08	0	0	0
t143		0.02	0	<0.02	0.07	0.02	0.02	0.01	0.02	<0.04	0	0.29	0.03	0.02	0.02
t145		0.02	<0	<0.01	0.01	0.01	0.01	0.01	0.04	<0.04	0	0.19	0.01	0.01	0.01
t155		0.05	0	0.02	0.01	0.04	0.06	0.03	<0.01	<0.03	0	0.38	0.02	0	0.01
t153		0.07	0	<0.01	0.03	0.02	0.07	<0.00	0.02	0	0	0.3	0.14	0.01	0.02
blank-nano-2		0	<0	<0.00	0	0	0.01	0.02	0.26	<0.03	<0.00	0.06	<0.00	<0.00	<0.00
m31888z	**S-1**	707.9	<106	53790.81	78.18	2.19	14.75	16.69	71.92	<30.31	<0.14	14.59	<0.39	<0.10	<0.22
m31889a	**S-2**	718.36	<124	54423.3	79.5	<2.39	13.22	14.06	40.46	<35.10	<0.16	6.51	<0.45	<0.12	53.05
m31890t	**S-3**	710.32	<112	46109.18	75.8	4.5	<7.18	11.19	23.69	<33.88	<0.16	2.16	<0.43	<0.11	<0.24
m31891x	**S-4**	723.87	<110	54827.74	79.84	<2.11	4.47	11.16	22.35	<31.17	<0.15	0.97	<0.40	<0.10	55.85
m31892b	**S-5**	686.57	0	51816.2	74.66	3.83	8.57	10.8	<13.79	<35.33	0.17	<0.71	<0.45	<0.11	51.02
m31893f	**S-6**	720.41	<102	52314.91	77.97	<2.19	19.06	9.37	<12.68	<32.67	<0.15	<0.65	<0.41	<0.11	55.22
m31894k	**S-7**	721.92	36	52394.81	77.64	<2.00	<6.25	9.05	<11.61	<29.84	<0.14	<0.60	<0.37	<0.10	52.86
m31895o	**S-8**	709.81	31	51498.94	77.49	3.51	<6.69	9	<12.42	<31.99	<0.15	<0.64	<0.40	<0.10	54.73
m31896s	**R-1**	675.77	55	49406.92	65.39	<1.91	<5.98	8.46	<11.10	<28.62	<0.13	<0.57	<0.36	<0.09	52.39
m31897w	**R-2**	710.07	68	51806.49	77.11	3.93	8.99	9.06	<12.04	<30.97	0.23	<0.62	<0.39	<0.10	52.61
m31898a	**R-3**	711.27	49	51918.18	77.51	2.45	25.42	9.22	<11.77	<30.33	<0.14	<0.60	<0.38	<0.10	52.98
m31899e	**R-4**	749.56	80	54034.74	84.16	8.83	10.72	9.57	<11.60	<29.82	0.16	<0.60	1.3	<0.10	46.64

APPENDIX B3 (IX screening test-contd.)

file =		0														
run =		waters														
owner =		MHossain														
date =		Feb 23 09	11:51 pm													
calculated:		26-Feb-09	13:55:54													
waters (w), biol. (b):		w														
avg diln g/g:		0.019452														
conc given in:		ppm														
conc in:		wet														
interference correction?															Cl	
intf. factor															48352	
ppm intf.															25	
lld - intf.															0.04	
lld - ppb/ppm															0.0009	
lld - blank		0.003	0.009	0.025	26		0.002	0.007	1.04	0.933	3.896	3.571	2.802	0.066	0.018	0.02
bk average					58976	10637										
Sample		**Li 7**	**Be**	**B**	**C**	**N**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ca 43**	**Ti**	**V**	**Cr 52**
name		ppm	ppm	ppm	ppm	cps	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
blanknano-1-Feb26		<0.00	<0.00	<0.00	<4	10810	<0.0	<0.0	<0	<0	<1	<1	<0	<0.01	<0.00	<0.00
t171		0.01	0	0.02	<5	10968	3	0	1	0	<1	10	6	<0.01	0	0
t143		0.02	0.01	0.03	<5	10322	9	0	9	<0	1	22	48	<0.01	0.03	0.04
m32015t	**CPF-1**	0.51	<1.51	0.24	<4200	11053	2	1.2	<167	<150	2844	<575	<451	<10.60	<2.83	<3.18
m32016a	**CPR-1**	<0.48	0.77	<4.19	<4450	10555	1	<1.1	<177	68	1735	<609	<478	<11.23	<3.00	<3.37
m32013f	**R-5**	<0.47	<1.59	58.26	<4408	10248	7572	10.7	<176	<158	69156	<603	52	<11.12	<2.97	<3.34
m32014m	**R-6**	<0.45	<1.53	51.26	<4234	9845	7473	11.0	<169	<151	66333	701	<454	<10.68	<2.87	<3.21
m32017i	**SX-R-1**	0.84	<1.44	62.36	<3987	9935	7434	8.5	<159	<143	72040	378	591	0.27	<2.70	<3.02

APPENDIX B3 (IX screening test-contd.)

			Ca	Ca	Ca	Ca		Cl		Br						
			232	5412	25357	9023		740301		-929						
			4	4	4	4		25		0						
			1.086	0.017	0.004	0.011		0.01		0.086						
			0.2246	0.003	0.0005	0.0007		0		0						
		0.003	0.178	0.005	0.003	0.008	0.017	0.014	0.016	0.11	0.001	0.001	0	0	0.002	0.001
Sample		**Mn**	**Fe 57**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Br**	**Se**	**Rb**	**Sr**	**Mo**	**Ag**	**Cd**	**Sn**
name		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
blanknano-1-Feb26		<0.00	<0	0	<0.00	0	0	<0.00	<0.00	<0.02	<0.00	0	<0.00	<0.00	<0.00	<0.00
t171		0.01	0	0	0.01	0.04	0.02	0	0.01	<0.02	0	0.08	0	0	0.01	0
t143		0.02	<0	0	0.07	0.04	0.02	0.01	0.02	<0.02	0	0.29	0.03	0.02	0.02	0
m32015t	**CPF-1**	<0.48	<22	7016.82	4.59	<1.32	5.06	<2.19	<2.50	<17.76	<0.20	<0.21	0.06	<0.08	<0.33	<0.22
m32016a	**CPR-1**	<0.51	<19	6757.03	<0.43	0.4	5.69	<2.32	<2.65	<18.83	<0.21	<0.22	<0.02	<0.08	<0.35	<0.23
m32013f	**R-5**	668.98	<23	45721.70	63.38	<1.38	9.2	7.82	<2.62	<18.65	<0.21	<0.22	0.05	<0.08	45.78	<0.23
m32014m	**R-6**	661.73	<15	45044.30	69.63	3.64	15.31	7.95	<2.52	<17.92	<0.20	<0.21	<0.02	<0.08	33.6	<0.22
m32017i	**SX-R-1**	474.72	<23	46478.60	71.72	2.56	9.01	7.95	<2.37	<16.87	<0.19	2.45	0.16	<0.07	40.26	<0.21

APPENDIX B4 (Extraction of metals –scoping test)

file =		0										
run =		waters										
owner =		MHossain										
date =		Mar 03 09	11:38 am									
calculated:		03-Mar-09	14:42:13									
waters (w), biol. (b):		w										
avg diln g/g:		0.013735										
conc given in:		ppm										
conc in:		wet										
interference correction?												
intf. factor												
ppm intf.												
lld - intf.												
lld - ppb/ppm												
lld - blank		0.008	0.062	0.013	171	0.099	1.359	11.546	3.595			
bk average					59152							
Sample		**Li 7**	**Be**	**B**	**C**	**Mg**	**Al**	**Cl**	**Ca 43**	**Mn**	**Fe 57**	**Co**
name		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
blanknano-1-Mar02		<0.00	<0.01	<0.00	<22	<0.0	<0.2	<1	1	<0.00	<0	0
t171		0	0	0.02	<23	2.4	<0.2	9	6	0.01	0	0
t143		0.01	0.01	0.04	<22	9.4	<0.2	23	50	0.02	<0	0
m32018p	**SX-r-2**	140.99	<7.20	277.99	<19860	5944.8	<157.7	<1340	628	154.27	<190	36865
m32019w	**CPR-2-1**	1.77	3.93	2.84	<20753	<12.0	<164.8	<1400	644	<3.12	<198	20606
m32020u	**CPR-2-2**	<0.99	<7.45	<1.56	27922	<11.9	<163.1	<1386	838	<3.08	<196	19700
m32021y	**CPR-2-3**	<1.11	<8.36	<1.75	<23063	<13.4	<183.1	<1556	157	<3.46	<220	20364
m32022d	**CPR-2-4**	<1.03	<7.74	<1.62	39090	<12.4	<169.7	<1441	492	<3.21	<204	18034
m32023i	**CPR-2-5**	<0.90	<6.73	2.75	<18580	<10.8	<147.5	<1253	31	<2.79	<177	17897
m32024m	**SX-R-2-1**	<0.93	<7.00	63.87	<19320	7819	<153.4	<1303	626	603.57	<184	46678
m32025r	**SX-R-2-2**	1.18	<6.44	55.66	<17761	7548	<141.0	<1198	658	548.44	<169	44940
m32026w	**SX-R-2-3**	<0.86	<6.49	62.12	40659	7529	<142.1	<1207	729	527.79	<171	47077
m32027a	**SX-R-2-4**	1.02	<5.84	61.3	43697	7440	<128.0	<1087	759	479.54	<154	45544
m32028f	**SX-R-2-5**	<0.92	<6.89	58.98	<18999	6945	<150.9	<1282	135	419.93	<181	43501
m32029k	**CPF-2**	<1.06	<7.98	6.75	<22022	<12.8	<174.9	<1485	767	<3.31	<210	18805
m32074m	**Co-elect-2**	<0.94	<7.04	68.13	<19431	7802.4	<154.3	<1311	503	674.59	<185	47068

APPENDIX B4 (Extraction of metals –scoping test)

Sample		Ni	Cu	Zn	As	Se	Br	Mo	Ag	Cd
name		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
blanknano-1-Mar02		<0.01	0	0.03	<0.00	<0.01	<0.00	<0.00	0	<0.00
t171		<0.01	<0.02	0	0	<0.02	0.01	0	0	0
t143		0.07	<0.02	0.02	0.01	<0.02	0.04	0.03	0.02	0.02
m32018p	**SX-r-2**	62.06	<16.89	<16.60	5.12	15.47	7.37	<0.91	<0.06	20.16
m32019w	**CPR-2-1**	<7.32	<17.64	<17.34	3.07	<14.34	<3.67	<0.95	<0.06	<0.60
m32020u	**CPR-2-2**	<7.25	<17.47	<17.17	2.52	<14.16	<3.63	<0.94	<0.06	<0.59
m32021y	**CPR-2-3**	<8.13	<19.61	3.51	4.08	<15.94	<4.08	<1.05	<0.07	<0.66
m32022d	**CPR-2-4**	<7.54	<18.17	26.29	3.31	<14.75	<3.78	<0.97	<0.06	<0.61
m32023i	**CPR-2-5**	<6.55	<15.80	5.8	3.09	<12.83	<3.29	<0.85	<0.06	<0.53
m32024m	**SX-R-2-1**	73.19	<16.43	8.8	8.39	<13.38	<3.42	<0.88	<0.06	45.14
m32025r	**SX-R-2-2**	67.49	<15.10	27.09	7.58	<12.29	<3.14	<0.81	<0.05	43.66
m32026w	**SX-R-2-3**	68.97	<15.22	9.47	8.52	115	<3.17	<0.82	0.14	43.59
m32027a	**SX-R-2-4**	68.51	<13.70	24.82	6.74	<11.17	<2.85	<0.73	<0.05	38.76
m32028f	**SX-R-2-5**	66.9	<16.15	<15.88	7.52	<13.15	<3.36	<0.87	<0.06	37.49
m32029k	**CPF-2**	<7.77	<18.72	6.34	4.61	<15.22	<3.89	<1.00	<0.07	<0.63
m32074m	**Co-elect-2**	71.78	<16.52	<16.24	8.58	<13.44	<3.44	<0.89	<0.06	52.74

APPENDIX B5 (Co-preloading and extraction of metals with Na-D2EHPA and Co-D2EHPA)

file =			0									
run =			waters									
owner =			RbStock/MHossain									
date =			Mar 18 09 15:37 pm									
calculated:			19-Mar-09	11:22:04								
waters (w), biol. (b):			w									
avg diln g/g:			0.031204									
conc given in:			ppm									
conc in:			wet									
interference correction?												
lld - ppb/ppm												
lld - blank			0.007	0.029	0.037	66	0.01	0.04				
bk average						50322						
Sample			**Li 7**	**Be**	**B**	**C**	**Mg**	**Al**	**Fe 54**	**Mn**	**Co**	**Sample**
name			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	diln g/g
blanknano-1			<0.00	<0.01	<0.01	34	<0.0	<0.0	<0	<0.00	<0.02	0.10995
t171			0.01	0	0.03	<20	2.6	<0.0	0	0.01	0	0.10175
t143			0.02	<0.01	0.03	<19	9.6	0	0	0.02	0.01	0.10695
t145			0.02	0.01	0.04	<20	8.1	0.1	0	0.02	0.01	0.10457
t155			0.03	<0.01	0.1	<18	11	0.1	0	0.05	<0.03	0.11341
t153			0.05	<0.01	0.1	<20	9	0	<0	0.07	<0.03	0.10159
Rb-1			<0.18	<0.78	<1.01	3198	<0.3	<1.1	<7	0.12	0.97	0.00114
Rb-2			<0.18	<0.78	<1.00	185	0	<1.1	<7	<0.08	<1.28	0.00115
Blank-nano-2		Sample#	<0.00	<0.01	<0.01	38	<0.0	<0.0	<0	<0.00	<0.01	0.10675
m32110r	M32110R	T#7	<1.93	<8.29	<10.63	37296	<2.9	<11.6	<73	<0.88	2291.94	0.00011
m32109w	M32109W	T#6	<1.93	<8.29	<10.63	32972	<2.9	<11.6	<73	<0.88	2642.13	0.00011
m32108p	M32108P	T#5	<1.99	<8.52	<10.93	42190	<2.9	0.2	<76	<0.91	4917.29	0.00010
m32107i	M32107I	T#4	<2.05	<8.80	<11.29	18591	<3.0	1	<78	<0.94	6941.11	0.00010
m32106a	M32106A	T#3	<1.99	<8.51	<10.92	47621	<2.9	0.9	<75	<0.90	9943.91	0.00011
m32105t	M32105T	T#2	<2.08	<8.93	<11.45	5710	<3.1	<12.5	<79	<0.95	12158.01	0.00010
m32104m	M32104M	T#1	<1.88	<8.06	<10.34	4648	<2.8	<11.2	<71	<0.86	16142.53	0.00011
m32103f	M32103F	CoSO4-syn	<1.84	<7.89	<10.12	32416	<2.7	<11.0	<70	<0.84	22876.26	0.00011
m32102y	M32102Y	SX-5-2.5	<1.60	<6.86	57.18	8223	6370.8	<9.6	<61	198.80	39995.54	0.00013
m32101r	M32101R	SX-5-2.4	<1.93	<8.27	57.09	2879	6868.5	<11.5	<73	220.61	42706.96	0.00011
m32100k	M32100K	SX-5-2.3	<1.93	<8.26	59.88	8741	7730.5	<11.5	<73	286.51	47996.18	0.00011
m32099e	M32099E	SX-5-2.2	<1.88	<8.05	56.19	39446	8168.4	<11.2	<71	390.38	52277.86	0.00011
m32098q	M32098Q	SX-5-2.1	<1.67	<7.14	59.89	30479	7941.8	<10.0	<63	424.60	50278.43	0.00013
m32097c	M32097C	Co-elect-2	<2.06	<8.83	68.62	5283	8588.6	18.5	<78	760.17	55668.00	0.00010
m32111m	M32111M	SX-R 3.1	<1.84	<7.90	61.8	35400	7467.6	<11.0	<70	218.23	56389.79	0.00011
m32112g	M32112G	SX-R 3.2	<1.96	<8.39	68.68	9739	7685.4	<11.7	<74	214.84	55176.14	0.00011
m32113a	M32113A	SX-R 3.3	<1.90	<8.13	53.29	31248	7205.3	<11.3	<72	193.30	51514.57	0.00011
m32114v	M32114V	SX-R 3.4	<2.04	<8.73	57.04	4884	6842.1	<12.2	<77	161.85	48531.60	0.00010
m32115p	M32115P	SX-R 3.5	<1.69	<7.26	63.49	<16783	7003.3	<10.1	<64	166.82	49877.06	0.00012

APPENDIX B5 (Co-preloading and extraction of metals with Na-D2EHPA and Co-D2EHPA)

Sample			Mo	Ag	Cd	Sn	Sb	I	Cs	Pb	Bi	U	Sample
name			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	diln g/g
blanknano-1			<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	0.10995
t171			0	0	0	0	0	0	<0.00	0	<0.00	0	0.10175
t143			0.03	0.02	0.02	0	0.02	0.01	<0.00	0.08	<0.00	0.01	0.10695
t145			0.01	0.01	0.01	0.01	0.01	0.01	0	0.01	<0.00	0	0.10457
t155			0.02	<0.00	0.01	0	0.02	0.01	<0.00	0.02	<0.00	0.01	0.11341
t153			0.14	0.01	0.02	0	0.03	0.01	<0.00	0.04	<0.00	0.01	0.10159
Rb-1			0.16	<0.02	<0.03	<0.04	<0.01	<0.20	<0.01	<0.05	<0.00	<0.01	0.00114
Rb-2			0.05	<0.02	<0.03	<0.04	<0.01	<0.20	<0.01	<0.05	<0.00	<0.01	0.00115
Blank-nano-2		Sample#	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	0.10675
m32110r	M32110R	T#7	<0.22	<0.22	<0.31	0.54	<0.15	<2.16	<0.08	<0.55	0.02	<0.06	0.00011
m32109w	M32109W	T#6	<0.22	<0.22	<0.31	<0.43	<0.15	<2.16	<0.08	<0.55	<0.01	<0.06	0.00011
m32108p	M32108P	T#5	<0.23	<0.23	<0.32	<0.44	<0.15	<2.23	<0.09	<0.57	<0.01	<0.06	0.00010
m32107i	M32107I	T#4	<0.23	<0.23	<0.33	<0.46	<0.16	<2.30	<0.09	<0.59	<0.01	<0.06	0.00010
m32106a	M32106A	T#3	<0.23	<0.23	<0.32	<0.44	<0.15	<2.22	<0.09	<0.57	<0.01	<0.06	0.00011
m32105t	M32105T	T#2	<0.24	<0.24	<0.33	<0.46	<0.16	<2.33	<0.09	<0.60	<0.01	<0.06	0.00010
m32104m	M32104M	T#1	<0.21	<0.21	<0.30	<0.42	<0.14	<2.10	<0.08	<0.54	<0.01	<0.05	0.00011
m32103f	M32103F	CoSO4-syn	<0.21	<0.21	<0.29	<0.41	<0.14	<2.06	<0.08	<0.53	<0.01	<0.05	0.00011
m32102y	M32102Y	SX-5-2.5	<0.18	<0.18	24.18	<0.36	<0.12	<1.79	<0.07	<0.46	<0.01	<0.05	0.00013
m32101r	M32101R	SX-5-2.4	<0.22	<0.22	25.05	<0.43	<0.15	<2.16	<0.08	<0.55	<0.01	<0.06	0.00011
m32100k	M32100K	SX-5-2.3	0.25	<0.22	30.93	<0.43	<0.15	<2.16	<0.08	<0.55	0.03	<0.05	0.00011
m32099e	M32099E	SX-5-2.2	<0.21	<0.21	35.94	<0.42	<0.14	<2.10	<0.08	<0.54	<0.01	<0.05	0.00011
m32098q	M32098Q	SX-5-2.1	<0.19	<0.19	42.23	<0.37	<0.13	<1.86	<0.07	<0.48	<0.01	<0.05	0.00013
m32097c	M32097C	Co-elect-2	<0.23	<0.23	54.62	<0.46	<0.16	<2.31	<0.09	<0.59	<0.01	<0.06	0.00010
m32111m	M32111M	SX-R 3.1	<0.21	<0.21	23.72	<0.41	<0.14	<2.06	<0.08	<0.53	<0.01	<0.05	0.00011
m32112g	M32112G	SX-R 3.2	<0.22	<0.22	25.17	<0.44	<0.15	<2.19	<0.08	<0.56	<0.01	<0.06	0.00011
m32113a	M32113A	SX-R 3.3	0.36	<0.22	24.54	<0.42	<0.14	<2.12	<0.08	<0.54	0.05	<0.05	0.00011
m32114v	M32114V	SX-R 3.4	<0.23	<0.23	21.91	<0.45	<0.15	<2.28	<0.09	<0.58	<0.01	<0.06	0.00010
m32115p	M32115P	SX-R 3.5	<0.19	<0.19	22.39	<0.38	<0.13	<1.89	<0.07	<0.48	<0.01	<0.05	0.00012

APPENDIX B6 (Kinetics of mangnanese extraction)

file =		0													
run =		waters													
owner =		MHossain													
date =		Mar 25 09	10:46 am												
calculated:		26-Mar-09	10:35:32												
waters (w), biol. (b):		w													
avg diln g/g:		0.069762													
conc given in:		ppm													
conc in:		wet													
interference correction?															
intf. factor															
ppm intf.															
lld - intf.															
lld - ppb/ppm															
lld - blank		0.004	0.014	0.01	88	0.002	0.027	0.359	22.293	1.87	1.364				
bk average					49384										
Sample		**Li 7**	**Be**	**B**	**C**	**Mg**	**Al**	**P**	**S**	**Cl**	**Ca 43**	**Mn**	**Fe 57**	**Co**	**Sample**
name		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	diln g/g
blanknano-1		<0.00	<0.01	<0.01	3	<0.0	<0.0	<0	<14	<1	<1	<0.00	<0	<0.02	0.11420
t171		0.01	0	0.04	<60	3.2	<0.0	0	6	13	8	0.01	0	0	0.10175
t143		0.02	0.01	0.05	<57	12.4	0	<0	<15	28	61	0.02	0	0.01	0.10695
t145		0.03	0.01	0.04	<59	9.3	0.1	<0	7	43	31	0.02	<0	0.01	0.10457
t155		0.04	<0.01	0.11	<54	14	0.1	<0	26	26	48	0.06	<0	<0.04	0.11341
t153		0.06	<0.01	0.1	<60	10	0	<0	14	38	30	0.08	<0	<0.03	0.10159
m32140m	SK-1	<2.32	<7.89	54.93	<50585	6373	<15.3	<207	56419	<1077	<785	186.09	<125	40260.15	0.00012
m32141v	SK-2	<2.13	<7.25	51.76	19786	5929	<14.1	<190	54063	<990	<722	178.21	<115	38723.58	0.00013
m32142d	SK-3	<2.11	<7.19	47.73	<46115	5653.8	<14.0	<188	59383	<981	<716	171.91	<113	33343.19	0.00013
m32143m	SK-4	<2.29	<7.81	55.05	<50070	5838.1	<15.2	<205	65194	<1066	<777	178.18	<124	34593.88	0.00012
m32144v	SK-5	<2.08	<7.07	42.83	<45351	5527	<13.7	<185	55071	<965	<704	168.21	<109	32891.55	0.00014
m32145d	AK-6	<2.29	<7.80	57.07	6829	6172.6	<15.2	<204	73650	<1064	<776	180.59	<127	35686.58	0.00012
m32146m	CK-1	210.17	<7.21	399.57	<46262	6707.1	<14.0	<189	74316	<985	<718	156.14	<113	48553.57	0.00013
m32147u	CK-2	<2.20	<7.50	58.45	<48064	6651.5	<14.6	<196	70357	<1023	<746	153.55	<116	49762.64	0.00013
m32148d	CK-3	<2.30	<7.84	60.49	9820	6980.6	<15.2	<205	78988	<1069	<780	161.12	<124	51105.94	0.00012
m32149l	CK-4	<1.98	<6.75	60.93	8005	6557.2	<13.1	<177	72278	<921	<672	154.02	<107	47578.13	0.00014
m32150t	CK-5	<2.02	<6.89	52.24	<44197	6684.2	<13.4	<181	62880	<941	<686	156.26	<105	49195.86	0.00014
m32151p	CK-6	<2.25	<7.66	55.01	<49139	6254.5	<14.9	<201	62367	<1046	<763	143.71	<119	46612.78	0.00013
m32152l	Co-elect-2	<2.15	<7.34	61.08	<47047	8497.7	<14.3	<192	77478	<1001	<730	732.56	<115	50335.08	0.00013
diw		<0.03	<0.10	<0.07	<613	<0.0	<0.2	<3	<156	<13	<10	<0.01	<2	<0.23	0.01000
m32146m dup		210.95	<7.21	376.83	<46262	6624	<14.0	<189	67161	<985	<718	152.40	<112	48750.48	0.00013
diw		<0.03	<0.10	<0.07	<613	<0.0	<0.2	<3	<156	<13	<10	<0.01	<2	<0.23	0.01000
diw		<0.03	<0.10	<0.07	<613	<0.0	<0.2	<3	<156	<13	<10				0.01000

APPENDIX B6 (Kinetics of mangnanese extraction)

Sample		Ag	Cd	Sn	Sb	I	Cs	Ba	La	Ce	Hg	Tl	Pb	Bi	U	Sample
name		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	diln g/g
blanknano-1		<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	0.11420
t171		0	0.01	0	0	0	<0.00	0.02	0	0	<0.00	0.01	0	<0.00	0	0.10175
t143		0.02	0.02	0	0.02	0.01	<0.00	0.1	0	0	<0.00	0.01	0.1	<0.00	0.01	0.10695
t145		0.01	0.01	0.01	0.01	0.01	0	0.04	0	0	<0.00	0.02	0.01	<0.00	0	0.10457
t155		<0.00	0.01	0	0.02	0	<0.00	0.03	0	0	<0.00	0.01	0.02	<0.00	0.01	0.11341
t153		0.01	0.02	0	0.03	0	<0.00	0.22	<0.00	0	<0.00	0.02	0.05	<0.00	0.01	0.10159
m32140m	SK-1	<0.18	24.03	<0.42	<0.22	<2.23	<0.07	0.35	<0.03	<0.02	<0.51	0.12	3.86	<0.08	<0.04	0.00012
m32141v	SK-2	<0.16	20.9	<0.39	<0.20	<2.05	<0.06	0.2	<0.03	<0.02	<0.46	<0.04	<0.04	<0.07	<0.03	0.00013
m32142d	SK-3	<0.16	21.36	<0.38	<0.20	<2.04	<0.06	0.35	<0.03	0.05	<0.46	<0.04	<0.04	<0.07	<0.03	0.00013
m32143m	SK-4	0.19	21.14	<0.42	<0.22	<2.21	<0.07	0.59	<0.03	0.03	<0.50	<0.05	<0.05	<0.08	<0.04	0.00012
m32144v	SK-5	<0.16	21.28	<0.38	<0.19	<2.00	<0.06	0.75	0.03	<0.02	<0.45	<0.04	<0.04	<0.07	<0.03	0.00014
m32145d	AK-6	<0.18	22.85	<0.42	<0.22	<2.21	<0.07	0.38	<0.03	0.02	<0.50	<0.05	<0.05	<0.08	<0.04	0.00012
m32146m	CK-1	<0.16	21.78	<0.39	<0.20	<2.04	<0.06	0.43	0.03	<0.02	<0.46	<0.04	0.23	<0.07	<0.03	0.00013
m32147u	CK-2	<0.17	20.2	<0.40	<0.21	<2.12	<0.06	0.82	<0.03	<0.02	<0.48	<0.05	<0.04	<0.07	<0.03	0.00013
m32148d	CK-3	<0.18	20.93	<0.42	<0.22	<2.22	<0.07	0.17	<0.03	<0.02	<0.50	<0.05	<0.05	<0.08	<0.04	0.00012
m32149l	CK-4	<0.15	20.52	<0.36	<0.19	<1.91	<0.06	1.06	<0.03	<0.02	<0.43	<0.04	0.22	<0.07	<0.03	0.00014
m32150t	CK-5	<0.15	20.34	<0.37	<0.19	<1.95	<0.06	0.17	<0.03	<0.02	<0.44	<0.04	<0.04	<0.07	<0.03	0.00014
m32151p	CK-6	<0.17	21.71	<0.41	<0.21	<2.17	<0.06	0.35	<0.03	<0.02	<0.49	<0.05	<0.04	<0.07	<0.03	0.00013
m32152l	Co-elect-2	<0.16	52.23	<0.39	<0.20	<2.08	<0.06	0.22	0.04	0.02	<0.47	<0.05	<0.04	<0.07	<0.03	0.00013
diw		<0.00	<0.01	<0.01	<0.00	<0.03	<0.00	0	<0.00	<0.00	<0.01	<0.00	<0.00	<0.00	<0.00	0.01000
m32146m dup		<0.16	21.45	<0.39	<0.20	<2.04	<0.06	0.41	<0.03	<0.02	<0.46	<0.04	0.18	<0.07	<0.03	0.00013
diw		<0.00	<0.01	<0.01	<0.00	<0.03	<0.00	0	<0.00	<0.00	<0.01	<0.00	<0.00	<0.00	<0.00	0.01000
		<0.00	<0.01	<0.01	<0.00	<0.03	<0.00	0	<0.00	<0.00	<0.01	<0.00	<0.00	<0.00	<0.00	0.01000

APPENDIX B7.1 (Stripping results: sample 1 ~ 5)

file =													
run =													
owner =													
date =													
calculated:			39994.6261										
waters (w), biol. (b):													
avg diln g/g:													
conc given in:													
conc in:													
interference correction?													
intf. factor													
ppm intf.													
lld - intf.													
lld - ppb/ppm													
lld - blank		0.02305523	0.00867978	0.00281555	0.00545556	0.02527128	0.23037612	16.8572698	0.008481				
bk average													
Sample		Li 6	Be	B	Mg	Al	P	S	Cr 52	Fe 54	Mn	Co	Sample
name		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	diln g/g
blank-nano-1		<0.01	<0.00	0.00431736	<0.0	<0.0	<0	<6	<0.00		<0	0.0081366	0.10671714
t171		<0.01	<0.00	0.02064486	2.45273688	0.01213844	<0	<7	0.00248667	0.01608821	0.01109751	0.00335433	0.10175236
t143		0.01467948	0.00536023	0.03266114	9.60994062	0.01594658	<0	1.12031123	0.03360988	0.20817011	0.01702056	0.00982576	0.10695276
m32445c	Str - 1	<7.13	<2.68	1.8318936	93.4698936	<7.8	180.529068	<5213	<2.62	<123	3.04106883	543.02032	0.00012774
m32446l	Str - 2	<7.04	<2.65	1.14501858	184.948291	<7.7	149.662985	<5150	<2.59	<122	6.30257485	1175.89997	0.00012929
m32447t	Str - 3	<7.80	<2.93	4.9722007	271.301212	<8.5	156.319881	<5700	<2.87	<135	9.75834857	1877.60854	0.00011683
m32448c	Str - 4	<8.17	<3.08	-0.898249	356.31299	<9.0	151.248078	<5975	<3.01	<141	14.244742	2757.71462	0.00011146
m32449k	Str - 5	<7.49	-1.1705946	<0.91	404.763203	<8.2	144.51788	<5475	<2.75	<130	17.5603086	3386.82374	0.00012164

APPENDIX B7.1 (Stripping results: sample 1 ~ 5)

Sample name		Ag ppm	Cd ppm	Sn ppm	Sb ppm	I ppm	Cs ppm	Ba ppm	La ppm	Ce ppm	Hg ppm	Pb ppm	Sample diln g/g
blank-nano-1		<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	0.00041077	7.33287E-06	<0.00	<0.00	2.5082E-05	0.10671714
t171		0.0021983	0.00471442	0.00118512	0.00240288	0.00229558	<0.00	0.01252533	3.92884E-05	0.00011762	<0.00	0.00093603	0.10175236
t143		0.0188557	0.01845481	0.00232236	0.01506918	0.01469858	<0.00	0.07533969	4.78015E-05	0.00010517	<0.00	0.07535184	0.10695276
m32445c	Str - 1	<0.09	<0.52	<0.22	<0.04	<4.11	<0.14	0.09538471	<0.00	<0.01	<0.21	<0.01	0.00012774
m32446l	Str - 2	<0.09	<0.52	<0.22	<0.04	<4.06	<0.13	0.08045023	<0.00	0.02429317	<0.21	<0.01	0.00012929
m32447t	Str - 3	<0.10	0.76907611	<0.24	<0.04	<4.50	<0.15	0.09925707	<0.00	<0.01	<0.23	<0.01	0.00011683
m32448c	Str - 4	<0.11	<0.60	<0.25	<0.04	<4.71	<0.16	0.07948339	<0.00	<0.01	<0.24	<0.01	0.00011146
m32449k	Str - 5	<0.10	0.86898095	<0.23	<0.04	<4.32	<0.14	0.07165251	<0.00	<0.01	<0.22	<0.01	0.00012164

APPENDIX B7.2 (Stripping results: sample 6 ~ 11)

file =		0												
run =		waters												
owner =		BuckleMNT/MHossain (w2252)												
date =		Aug 03 09 12:35 pm												
calculated:		04-Aug-09	9:47:29											
waters (w), biol. (b):		w												
avg diln g/g:		0.047606												
conc given in:		ppb												
conc in:		wet												
interference correction?													Cl	
intf. factor													57451	
ppm intf.													25	
lld - intf.													8.318	
lld - ppb/ppm													0.0948	
lld - blank		2.108	3.494	21.592	1.626	2.512	1215.808	196.067	46776.791	3625.131	908.841	38.815	5.938	11.486
bk average														
Sample		**Li 7**	**Be**	**B**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ca 43**	**Ti**	**V**	**Cr 52**
name		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
bnano-1		<3.65	<6.05	<37.37	4.6	<4.3	<2104	<339	<80962	<6274	<1573	<67.18	<10.28	<19.88
t171		4.64	<1.61	18.99	2474	14.8	1420	<91	<21609	9179	6226	<17.93	<2.78	<5.31
t143		15.24	8.2	26.79	9202	17.1	9878	<91	<21734	21733	48775	<18.03	23.56	32.67
t145		23.21	7.58	36.93	7698	48.5	4856	<78	2217	38374	27700	<15.47	8.64	12.45
t155		31.13	<1.46	84.1	10719	55.4	4772	<82	17332	22804	41695	<16.25	21.81	8.28
t153		48.44	<1.73	83.47	7974	30	2465	<97	7743	32203	25503	<19.20	14.82	13.62
m32526j	**STR-6**	<564.32	<935.64	1301.65	690617	<672.5	<325536	118668	3956945	<970639	<243345	462	<1589.51	<3075.50
m32527d	**STR-7**	<576.26	206.77	138.28	1250339	431	23503	35579	9761416	37236	80451	<10613	<1623.87	<3140.60
m32528x	**STR-8**	<549.25	596.29	555.23	1287288	1677.3	79532	32163	13401634	130918	151424	2862	<1548.17	<2993.36
m32529s	**STR-9**	<601.02	97.07	1733.86	1279240	7229.4	150284	36895	21877328	52115	228583	4533	<1693.69	<3275.51
m32530p	**STR-10**	<494.78	571.14	1416.44	1223526	9498.6	98107	22174	27446752	<851034	167794	2425	<1393.90	<2696.53
m32531h	**STR-11**	<524.10	925.46	1566.51	1234978	10814.8	152991	24366	41580020	236034	229267	3568	<1477.79	<2856.31
m32524u	**CF-2**	<521.31	752.88	63133.98	7941520	11895.5	157707	18950	74474443	106702	232754	3400	<1469.34	<2841.09
m32525p	**SXR-2**	<443.87	330.43	57131.5	6367294	2005	100395	22853	68558817	159920	159526	1876	<1251.38	<2419.04

APPENDIX B7.2 (Stripping results: sample 6 ~ 11)

			Ca	Ca	Ca	Ca		Cl		Br				
			373	8992	-41731	48180		196837		352				
			4	4	4	4		25		0				
			127.641	9.349	1.471	1.803		0.802		15.737				
			0	0	0.0212	0.2874		0		78.5809				
		0.484	211.956	9.702	1.386	0.642	3.9	2.311	7.377	3.868	0.225	0.101	0.675	0.364
Sample		**Mn**	**Fe 57**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Br**	**Se**	**Rb**	**Sr**	**Mo**	**Ag**
name		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
bnano-1		<0.84	71	<16.79	30.13	8.07	9.75	<4.00	<12.77	<6.70	<0.39	0.23	<1.17	<0.63
t171		11.71	<98	4.78	7.07	5.71	21.8	2.56	12.55	<1.83	1.1	75.61	1.57	2.35
t143		16.75	264	9.87	64.57	21.41	19.04	12.97	36.63	5.32	0.84	278.05	31.29	19.36
t145		19.08	131	5.96	12.38	10.53	9.55	7.9	50.01	1.9	2.05	181.63	7.99	7.28
t155		51.23	105	21.34	10.08	40.31	64.05	30.45	15.62	5.81	0.94	361.23	23.42	0.1
t153		70.24	108	<4.80	29.66	23.7	67.72	<1.14	24.26	<2.00	0.82	289.43	132.69	6.19
m32526j	**STR-6**	41998	4772	7377016	9046	187	1075	1027	<1975	<1032	<60.25	<26.92	95.51	<97.37
m32527d	**STR-7**	600267	<57953	11473441	11181	1323	2506	1717	<2017	<1059	<61.52	<27.49	<184.48	<99.44
m32528x	**STR-8**	689208	8560	11773484	46168	1083	3656	1468	<1922	<1009	<58.64	<26.20	269.52	<94.77
m32529s	**STR-9**	691589	13749	11331909	9898	1141	2581	1596	<2104	<1105	<64.17	50.04	<192.40	<103.71
m32530p	**STR-10**	666407	23686	11183458	9427	1038	2642	1327	<1732	<908	<52.82	<23.60	28.45	<85.38
m32531h	**STR-11**	657938	12224	11030970	9165	1297	2565	1511	<1834	<964	<55.95	48.73	<167.78	<90.43
m32524u	**CF-2**	699171	28350	54577879	81793	1468	2240	7364	<1825	<957	<55.66	79.47	<166.89	<89.95
m32525p	**SXR-2**	163093	27025	54046826	75230	1158	16403	7194	<1554	<816	<47.39	116.35	<142.10	<76.59

APPENDIX B7.2 (Stripping results: sample 6 ~ 11)

Sample name		Cd ppb	Sn ppb	Sb ppb	I ppb	Cs ppb	Ba ppb	La ppb	Ce ppb	Hg ppb	Tl ppb	Pb ppb	Bi ppb	U ppb	Sample diln g/g
bnano-1		<0.83	<0.45	<0.23	<55.02	<0.04	3.58	<0.08	0.04	<0.88	<0.13	0.8	<0.20	<0.06	0.027505
t171		4.35	1.33	2.38	<14.69	0.03	12.19	0.09	0.11	<0.24	7.24	1.25	<0.05	1.17	0.103051
t143		18.24	2.4	15.94	18.64	0.02	75.31	0.07	0.12	<0.24	8.99	75.03	<0.05	10.69	0.102458
t145		9.22	4.81	8.2	20.18	0.09	33.53	0.07	0.11	<0.20	14.34	11.53	<0.05	1.01	0.119414
t155		11.66	1.36	17.09	<13.31	0.02	21.31	0.06	0.1	<0.21	9.24	18.65	<0.05	7.32	0.113703
t153		15.61	3.34	24.58	<15.72	0.02	169.81	0.04	0.06	<0.25	19.24	43.04	<0.06	6.79	0.096261
m32526j	**STR-6**	3173	<69.19	<35.00	460	11.88	234.17	14.15	<5.51	<136.71	<20.71	32.57	<31.25	<9.76	0.000178
m32527d	**STR-7**	35264	<70.66	<35.74	490	<5.93	23.88	16.13	<5.62	<139.61	<21.15	100.51	<31.91	<9.97	0.000174
m32528x	**STR-8**	39184	<67.35	<34.06	403	<5.65	50.91	36.6	9.64	<133.06	<20.16	104.82	<30.41	<9.50	0.000183
m32529s	**STR-9**	39155	<73.69	<37.27	297	9.04	3312.14	24.75	18.12	<145.60	<22.06	137.83	<33.28	<10.40	0.000167
m32530p	**STR-10**	37336	<60.67	<30.69	<7463	<5.09	51.15	40.8	24.41	<119.87	<18.16	78.45	<27.40	<8.56	0.000203
m32531h	**STR-11**	37878	<64.26	<32.50	<7905	<5.40	49.16	75.15	94.57	<126.97	<19.24	171.2	<29.02	<9.07	0.000191
m32524u	**CF-2**	52188	<63.92	<32.33	<7863	10.41	81.55	34.11	40.85	<126.29	<19.13	58.55	<28.87	<9.02	0.000192
m32525p	**SXR-2**	20173	61.03	<27.53	<6695	<4.57	187.22	11.78	15.41	<107.53	<16.29	94.96	<24.58	<7.68	0.000226

APPENDIX C

APPENDIX C1 (Sample calculation for separation factor of Mn and Co)

As we know from Equation 2.1 in Chapter - 2, the Distribution ratio is,

$$D = \frac{(w - w_1) \,/\, V_o}{w_1 \,/\, V_a}$$

Where, w represents the original weight of the solute in the aqueous phase and w_1 represent the final weight of the solute in the aqueous phase, Vo and Va are the volume of the organic and the aqueous solution respectively.

In terms of concentration, we can write the above equation as'

$$D = \frac{\text{Conc. of metals in organic phase}}{\text{Conc. of metals in aqueous phase,}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(A)}$$

and

$$\text{Separation factor, } \beta = \frac{\text{Distribution ratio of Mn}}{\text{Distribution ratio of Co}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(B)}$$

For pH 3.5

$$D_{Mn} = \frac{[M_n]_O \text{ (ppm)}}{[M_n]_A \text{ (ppm)}} = \frac{542}{218} = 2.49$$

$[M_n]_A$ = 218 ppm (from ICP-MS result)
$[M_n]_O = [M_n]_F - [M_n]_A = 760 - 218 = 542$

$$D_{co} = \frac{[Co]_O \text{ (ppm)}}{[Co]_A \text{ (ppm)}} = \frac{279}{55390} = 0.005$$

$$\beta_{Mn\text{-}Co} = \frac{D_{Mn}}{D_{co}} = \frac{2.49}{0.005} = 498$$

APPENDIX C2 (Sample calculation for separation factor of Cd and Co)

Following the same equations given in Appendix – C1,

For pH 3.5

$$D_{Cd} = \frac{[Cd]_O\,(ppm)}{[Cd]_A\,(ppm)} = \frac{31.28}{23.72} = 1.32$$

$[Cd]_A = 23.72$ ppm (from ICP result-Appendix B5)
$[Cd]_O = [Cd]_F - [Cd]_A = 55 - 23.72 = 31.28$

$$D_{co} = \frac{[Co]_O\,(ppm)}{[Co]_A\,(ppm)} = \frac{278}{55390} = 0.005$$

$$\beta_{Cd\text{-}Co} = \frac{D_{Mn}}{D_{co}} = \frac{1.32}{0.005} = 264$$

APPENDIX D

Statictics with 4 data point (5,10,60 & 120)	
Mean	58.15
Standard Error	1.398254865
Median	59.315
Mode	#N/A
Standard Deviation	2.796509729
Sample Variance	7.820466667
Kurtosis	3.675807704
Skewness	-1.901458018
Range	5.99
Minimum	53.99
Maximum	59.98
Sum	232.6
Count	4
Confidence Level(95.0%)	4.449871027

Relative Standard Deviation, RSD (%) = 4.8%

Statictics with all data points	
Mean	58.01666667
Standard Error	0.969101531
Median	59.175
Mode	#N/A
Standard Deviation	2.37380426
Sample Variance	5.634946667
Kurtosis	0.284950266
Skewness	-1.269889597
Range	5.99
Minimum	53.99
Maximum	59.98
Sum	348.1
Count	6
Confidence Level (95.0%)	2.491154792

Relative Standard Deviation, RSD (%) = 4.1%

APPENDIX E

APPENDIX E1

Brief Procedure of Data Measurement by ICP-MS and Statistical Summary

ICPMS (Inductively Coupled Plasma Mass Spectrometry) was used in this experiment to measure the metal concentrations, in the aqueous sample solutions, under the, 'water sample protocols'. During analysis with the ICP-MS, typical sample sequence had 5 calibration standard solutions (A, B, C, D, E), followed by blank count, and unknown given sample. At first, CPS (count per second) was measured based on the standard solutions, and then for the given samples. The sensitivity (cps/ppb) of the calibration standard-A (STDA) from the repeated measurement was used to calculate the concentration of elements (ppb) in the sample solutions that went into ICP-MS. The other calibration standards (STDB) contained interfering elements. The counts from the calibration blanks were averaged and subtracted (corrected) from all the measurements prior to further processing. The dilution factor was used to calculate the concentration of elements in the original samples. Drift was monitored from the internal standard elements (Sc, In, Rh and Re) and corrected for the measurements.

APPENDIX E2

Table E2

CPS data

Mhossain Time: Mar 25 09 10:46 am			Li 7	Be 9	Mn 55	Fe 57	Co 59	Rh 103	Ag 107	Cd 111
STDA		1	2259	639	8949	4725	6982	49828	2749	3780
STDB		2	78	58	339	3310	449	48863	50	48
STDC		3	72	63	294	3190	333	50132	45	36
STDD		4	74	66	299	3231	279	51161	44	44
STDE		5	80	64	304	3249	206	49554	42	43
bk		6	77	60	304	3259	188	50569	41	34
blanknano-1		7	72	68	276	3209	201	49226	50	44
t171		8	136	68	1355	3214	535	46714	184	115
t143		9	298	95	1940	3751	1491	45692	1350	336
t145		10	380	93	2070	3412	915	50037	522	171
t155		11	543	62	5494	3499	2518	48232	51	221
t153		12	727	61	6856	3355	217	47772	456	266
m32140m	**SK-1**	13	76	65	17089	3090	3288222	48229	43	392
m32141v	**SK-2**	14	81	68	17978	3079	3476721	48611	46	376
STDA		15	2400	681	9463	4771	7526	48384	2943	4112
STDB		16	87	56	231	3256	458	48366	43	31
STDC		17	67	67	213	3063	359	48731	41	42
STDD		18	67	60	218	3116	361	46671	39	41
STDE		19	74	66	266	3156	264	47404	39	40
bk		20	63	59	223	3079	249	47946	49	38
null1		21	69	67	18082	3100	3475379	47411	49	403
null2		22	74	67	16682	3056	3223864	46906	46	383
null3		23	90	64	18005	3071	3497565	45900	45	388
null4		24	71	70	16565	3079	3223579	47006	42	358
null5		25	3049	67	16046	3086	5032945	46570	42	422
null6		26	75	74	13104	2956	4099134	49970	47	297
null7		27	76	71	15175	3110	4724402	46463	52	386
null8		28	71	66	16366	3083	5087454	46786	48	379
STDA		29	2379	655	9232	4687	8140	45566	2749	3802
STDB		30	83	68	269	3217	1614	44482	39	46
STDC		31	76	75	270	3086	1004	48115	52	48
STDD		32	77	74	285	3019	866	48225	41	42
STDE		33	73	56	306	3086	712	45359	45	32
bk		34	85	65	262	2984	653	45664	43	41
null9		35	79	76	17011	3048	5341989	45772	42	412
null10		36	74	71	13822	3037	4461057	45237	48	359
null11		37	81	69	71166	2984	4816794	44761	39	923
null12		38	68	58	242	2964	1253	45400	41	38
null13		39	72	69	255	2983	1322	46867	51	35
null14		40	3027	63	16105	3038	4974829	46997	44	396

diw		41	68	58	242	2964	1253	45400	41	38
diw		42	68	58	242	2964	1253	45400	41	38
STDA		43	2328	673	9106	4632	[illegible]	45760	2755	3930
STDB		44	69	69	287	3162	1738	45116	45	37
STDC		45	83	72	249	2993	1453	46581	38	43
STDD		46	81	64	271	3047	1316	46559	47	39
STDE		47	72	62	269	2958	1022	45424	39	38
bk		48	70	77	230	3011	910	46334	38	37
m32142d	**SK-3**	49	76	62	17924	2940	3442009	45307	42	389
m32143m	**SK-4**	50	70	80	16555	2939	3184579	44567	50	352
m32144v	**SK-5**	51	67	60	17943	2984	3470423	45216	49	393
m32145d	**AK-6**	52	72	68	16144	2946	3165039	43554	44	369
m32146m	**CK-1**	53	2967	66	0	2950	7	45661	41	397
m32147u	**CK-2**	54	83	81	15247	2947	4880977	45203	43	355
m32148d	**CK-3**	55	69	70	14854	2959	4660947	44707	45	348
m32149l	**CK-4**	56	78	59	16744	2986	5121635	45198	40	396
STDA		57	2379	626	9079	4486	[illegible]	45237	2754	3969
STDB		58	67	71	290	3091	2323	45439	35	42
STDC		59	75	66	251	2860	2079	44906	36	35
STDD		60	68	67	245	2900	1930	45712	46	42
STDE		61	62	74	289	2936	1645	45408	33	36
bk		62	74	68	254	2820	1481	45561	41	35
m32150t	**CK-5**	63	79	57	17792	2958	5494860	46322	47	404
m32151p	**CK-6**	64	73	75	14216	2942	4507903	44457	41	374
m32152l	**Co-elect-2**	65	86	61	73692	2856	5038578	45464	44	907
diw		66	72	50	262	2832	2470	44927	48	36
newtube w diw		67	79	58	259	2807	2142	44683	44	44
diw		68	82	69	231	2761	1347	44422	33	39
diw		69	82	69	231	2761	1347	44422	33	39
diw		70	82	69	231	2761	1347	44422	33	39
STDA		71	2323	659	9066	4482	[illegible]	42821	2715	3878
STDB		72	76	58	280	2900	2255	43938	50	41
STDC		73	64	66	256	2787	1996	44205	45	37
STDD		74	80	68	268	2863	1867	45320	41	42
STDE		75	74	59	276	2833	1509	43313	42	35
bk		76	66	63	269	2792	1332	44779	38	34

APPENDIX E2.1

Table E2.1

Sample calculation for the measurement of the concentrations (Mn, Cd and Co) of metals baesd on cps-data (Appendix E2).

Repeated Std.A	Std. A for Mn	Blank data for Mn	Std. A for Co	Blank data for Co	Std. A for Cd	Blank data for Cd
1	8949	304	6982	188	3780	34
2	9463	223	7526	249	4112	38
3	9232	262	8140	653	3802	41
4	9106	230	8459	910	3930	37
5	9079	254	9118	1481	3985	35
6	9066	269	8879	1332	3878	34
AV=	9149.17	257	8184	802.17	3914.5	36.50

CPS count (Appendix E2) for ICPMS sample # m32146m and research sample # CK-1 of Appendix B6.

Mn CPS = 16020 Co CPS= 4931577

Cd CPS = 397

From Appendix E5, the standard concentration for metals (same for all run)

Std. conc. of Mn = 11.6 ppb
Std. conc. of Co= 10.2 ppb
Std. conc. of Cd= 31.4 ppb

As per described procedures (Appendix E), metal concentration (ppb) is measured as follows:

Conc. (ppb)=(Element CPS - blank av.)* Std. conc. of element/(Std. CPS - blank av.)

Using MS Excel, the concentration of metals in the diluted solution are obtained as follows:

Mn conc. (ppb) = 20.6634422
Co conc. (ppb) = 6568.499158
Cd conc. (ppb) = 2.907332734

Dilution factor (D.F.)
[Appendix-E4] = 0.000133

Appendix E2.1-contd.

Conc. of metals in the original solution (dividing the calculated conc. by the D.F.)

Mn conc. (ppb) = 155364.23
Co conc. (ppb) = 49387211.71
Cd conc. (ppb) = 21859.64

Error comparison for the sample calculated result with that of measured data by the ICP-MS software (LOTUS 1-2-3/MS Excel) - Appendix B6

Original concentration of metals	**From sample calculation**	**From ICP-MS cal.(Appendix B6)**	**Error (%)**
Mn conc. (ppm) =	155.36	156.14	-0.50
Co conc. (ppm) =	49387.21	48553.57	1.72
Cd conc. (ppm) =	21.86	21.78	0.37

APPENDIX E2.10

Table E2.10

Repeated Standard CPS summary data for Mn, Co and Cd-kinetic study

(Extracted from Appendix E2.1)			
Repeated Std.A	**Std. A for Mn**	**Std. A for Co**	**Std. A for Cd**
1	8949	6982	3780
2	9463	7526	4112
3	9232	8140	3802
4	9106	8459	3930
5	9079	9118	3985
6	9066	8879	3878

APPENDIX E2.11

Table E2.11

Statistical data for Mn	
Mean	9149.166667
Standard Error	72.82921422
Median	9092.5
Mode	#N/A
Standard Deviation	178.3944132
Sample Variance	31824.56667
Kurtosis	1.648834013
Skewness	1.186672031
Range	514
Minimum	8949
Maximum	9463
Sum	54895
Count	6
Confidence Level (95.0%)	187.2134551
Relative Standard Deviation, (RSD) %	1.95

APPENDIX E2.12

Table E2.12

Statistical data for Co	
Mean	8184
Standard Error	332.2002408
Median	8299.5
Mode	#N/A
Standard Deviation	813.7210824
Sample Variance	662142
Kurtosis	-1.021207233
Skewness	-0.473469865
Range	2136
Minimum	6982
Maximum	9118
Sum	49104
Count	6
Confidence Level (95.0%)	853.9479045
Relative Standard Deviation, (RSD) %	9.94

APPENDIX E2.13

Table E2.13

Statistical data for Cd	
Mean	3914.5
Standard Error	50.42998447
Median	3904
Mode	#N/A
Standard Deviation	123.5277297
Sample Variance	15259.1
Kurtosis	-0.130681465
Skewness	0.660865603
Range	332
Minimum	3780
Maximum	4112
Sum	23487
Count	6
Confidence Level (95.0%)	129.634402
Relative Standard Deviation, (RSD) %	3.16

APPENDIX E3

Table E3

Monday	Element	Mn	Fe	Fe	Co	Ni	Cu	Cd
August 03 2009	Isotope	**55**	**56**	**57**	**59**	**60**	**63**	**111**
12:35:21	diw	77	227727	2750	75	69	518	26
2009 12:42:26	STDA	[illegible]	358636	5736	[illegible]	5598	13845	[illegible]
2009 12:49:31	STDB	148	240517	3055	571	106	462	30
2009 12:56:37	STDC	119	238302	2795	365	75	302	33
2009 13:03:44	STDD	118	233449	2856	258	85	360	31
2009 13:10:53	STDE	154	238493	2814	188	97	291	32
2009 13:17:59	bk	91	229703	2683	78	119	394	29
2009 13:25:03	bnano-1	115	227376	2736	78	318	529	30
2009 13:32:07	t171	1691	229185	2905	720	290	754	121
2009 13:39:12	t143	2362	227972	3536	1811	1666	1760	410
2009 13:46:17	t145	3089	212462	3160	1268	451	1179	254
2009 13:53:22	t155	7773	212894	3144	3411	365	3168	300
2009 14:00:27	t153	9102	217771	3013	92	791	1794	340
2009 14:07:33	buckleMN T Tap	231	214057	3029	85	297	1821	26
2009 14:14:39	buckleMN T Tap dup	311	211360	3020	81	318	1863	26
2009 14:21:45	diw	82	210096	2597	78	86	516	25
2009 14:28:50	STDA	[illegible]	348522	5586	1894	5421	13411	[illegible]
2009 14:35:55	STDB	157	228863	2922	562	96	473	29
2009 14:43:01	STDC	125	229450	2726	353	77	315	30
2009 14:50:09	STDD	135	230148	2732	246	83	357	23
2009 14:57:17	STDE	156	237734	2761	188	94	280	27
2009 15:04:23	bk	93	229849	2647	77	125	414	29
2009 15:11:27	m32526j	10322	210708	2678	1563668	519	433	151
2009 15:18:32	m32527d	140443	184353	2593	2336974	590	543	1333
2009 15:25:36	m32528x	165369	175255	2600	2459176	2102	511	1512
2009 15:32:41	m32529s	149637	167893	2591	2137189	500	501	1384
2009 15:39:46	m32530p	175307	163494	2656	2560042	559	510	1569

2009 15:46:52	m32531h	161023	157994	2568	2352122	515	525	1501
2009 15:53:57	m32524u	170907	151516	2628	11612143	3692	539	2038
2009 16:01:03	m32525p	47495	149432	2682	13676641	4029	533	951
2009 16:08:09	diw	99	144125	2608	1207	83	473	28
2009 16:15:14	STDA	8	264938	5378	11	5123	12560	6291
2009 16:22:19	STDB	151	155317	2886	827	89	419	26
2009 16:29:25	STDC	125	154467	2673	661	81	306	28
2009 16:36:33	STDD	123	153718	2669	552	94	324	29
2009 16:43:41	STDE	145	157771	2626	476	100	268	25
2009 16:50:48	bk	108	155955	2628	384	111	387	31
2009 16:57:52	diw	97	153719	2629	369	93	583	33

APPENDIX E3.1

Table E3.1

Statistical data of sensitivity measurement for Mn-stripping study	
Mean	15507.33333
Standard Error	354.4170487
Median	15709
Mode	#N/A
Standard Deviation	613.8683355
Sample Variance	376834.3333
Kurtosis	#DIV/0!
Skewness	-1.318782842
Range	1177
Minimum	14818
Maximum	15995
Sum	46522
Count	3
Confidence Level (95.0%)	1524.933482
Relative Standard Deviation, (RSD) =	4%

APPENDIX E3.2

Table E3.2

Statistical data of sensitivity measurement- Co stripping	
Mean	11969
Standard Error	236.5297726
Median	11894
	#N/A
Standard Deviation	409.6815837
Sample Variance	167839
Kurtosis	#DIV/0!
Skewness	0.796201123
Range	809
Minimum	11602
Maximum	12411
Sum	35907
Count	3
Confidence Level (95.0%)	1017.705472
Relative Standard Deviation, (RSD) =	3.4%

APPENDIX E3.3

Table E3.3

Statistical data of sensitivity measurement- Cd stripping	
Mean	6606.666667
Standard Error	168.9717268
Median	6660
Mode	#N/A
Standard Deviation	292.6676158
Sample Variance	85654.33333
Kurtosis	#DIV/0!
Skewness	-0.792810576
Range	578
Minimum	6291
Maximum	6869
Sum	19820
Count	3
Confidence Level (95.0%)	727.0266614
Relative Standard Deviation (RSD) =	4.4%

APPENDIX E4 (Conc. of std. solutions, dilution factor of samples, lower detection limits of metals)

Concentration of Standards A,B,C,D,E (ppb):				(same for all runs)									
Run	Entered		Li	Be	B	C	Mg	Mn	Co	Ni	Ag	Cd	
Aug01a			21.8	21.9	52.5		52.8	11.6	10.2	22	5.2	31.4	
Aug01b													
Aug01c													
Aug01d													
Jul28a						75465.8							
Mar. 25, 2009													
Dilution		Weights			Weights								
g/g													
final Dilution	Sample No.	Wt. of Sample (g)	Wt of nitric acid (g)		Wt solid (g)	Final Vol (g)	1st dilution						
0.114198	blanknano-1	1.1618	9.0118										
0.101752	t171	12.31	108.67										
0.106953	t143	12.86	107.38										
0.104569	t145	12.93	110.72										
0.113411	t155	14.19	110.93										
0.101591	t153	12.39	109.57										
0.000121	m32140m	0.1005	10.0986		0.1252	10.1797	0.012298987						
0.000132	m32141v	0.1082	10.1548		0.1272	10.1703	0.012507006						
0.000133	null1	0.1069	10.1129		0.1299	10.221	0.012709128						
0.000122	null2	0.1061	10.2033		0.1212	10.1876	0.011896816						
0.000135	null3	0.1077	10.1084		0.1332	10.3879	0.012822611						
0.000123	null4	0.1051	10.105		0.1232	10.3455	0.011908559						
0.000133	null5	0.1042	10.1927		0.1335	10.1947	0.01309504						
0.000128	null6	0.1045	10.1638		0.1273	10.1571	0.012533105						
0.000122	null7	0.104	10.2118		0.1235	10.2046	0.012102385						
0.000142	null8	0.1053	10.1461		0.14	10.1488	0.013794734						
0.000139	null9	0.1068	10.1226		0.1349	10.1538	0.013285666						
0.000125	null10	0.105	10.1119		0.1306	10.7583	0.012139464						
0.000130	null11	0.1074	10.1281		0.128	10.3072	0.012418504						
#DIV/0!	null12	0.1	9.9				#DIV/0!						
#DIV/0!	null13	10	0				#DIV/0!						

APPENDIX E4 (Conc. of std. solutions, dilution factor of samples, lower detection limits of metals)

0.000133	null14	0.1042	10.1927		0.1335	10.1947	0.01309504						
#DIV/0!	diw	0.1	9.9				#DIV/0!						
#DIV/0!	diw	0.1	9.9				#DIV/0!						
0.000133	m32142d	0.1069	10.1129		0.1299	10.221	0.012709128						
0.000122	m32143m	0.1061	10.2033		0.1212	10.1876	0.011896816						
0.000135	m32144v	0.1077	10.1084		0.1332	10.3879	0.012822611						
0.000123	m32145d	0.1051	10.105		0.1232	10.3455	0.011908559						
0.000133	m32146m	0.1042	10.1927		0.1335	10.1947	0.01309504						
0.000128	m32147u	0.1045	10.1638		0.1273	10.1571	0.012533105						
0.000122	m32148d	0.104	10.2118		0.1235	10.2046	0.012102385						
0.000142	m32149l	0.1053	10.1461		0.14	10.1488	0.013794734						
0.000139	m32150t	0.1068	10.1226		0.1349	10.1538	0.013285666						
0.000125	m32151p	0.105	10.1119		0.1306	10.7583	0.012139464						
0.000130	m32152l	0.1074	10.1281		0.128	10.3072	0.012418504						
#DIV/0!	diw	0.1	9.9				#DIV/0!						
#DIV/0!	newtube w diw	10	0				#DIV/0!						
#DIV/0!	diw	0.1	9.9				#DIV/0!						
#DIV/0!	diw	0.1	9.9				#DIV/0!						
#DIV/0!	diw	0.1	9.9				#DIV/0!						
		Li 6	Li 7	Cr 52	Cr 53	Fe 54	Mn	Fe 56	Fe 57	Co	Ni	Ag	Cd
		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
Lower limit of detection		23.374	2.108	11.486	16.231	220.276	0.484	3003.747	211.956	9.702	1.386	0.364	0.479

APPENDIX E5 (RSD of standard data, measured by ICP-MS)

		Li 6	Li 7	Sc 45	Fe 54	Mn 55	Fe 56	Fe 57	Co 59	Rh 103	Ag 107	Cd 111	Re 187	Th 232
Tube	Sample	Li 6	Li 7		Fe 54	Mn	Fe 56	Fe 57	Co		Ag	Cd		
name	name	ppb	ppb		ppb	ppb	ppb	ppb	ppb		ppb	ppb		
	Lower limit of detection	23.374	2.108		220.276	0.484	3003.747	211.956	9.702		0.364	0.479		
Calibration standard solutions used (in ppb):														
Run	Entered	Li	Li	Sc	Fe	Mn	Fe	Fe	Co	Rh	Ag	Cd	Re	Th
STDA	Mar31a	21.8	21.8	Internal	121.4	11.6	121.4	121.4	10.2	Internal	5.2	31.4	Internal	Internal
STDB	Mar31b			Standard						Standard			Standard	Standard
STDC	Mar31c			element						element			element	element
STDD	Mar31d													
STDE	Dec02a													
meas. sens CPS avg*		353	3405	76563	10591	15507	324032	5567	11969	41512	4596	6607	28664	57602
*** from repeated measurement of element in the calibration standard**														
std dev		27	209	2265	654	614	51426	180	410	1107	206	293	432	804
rsd**		**7.6%**	**6.1%**	**3.0%**	**6.2%**	**4.0%**	**15.9%**	**3.2%**	**3.4%**	**2.7%**	**4.5%**	**4.4%**	**1.5%**	**1.4%**
(rsd - indicates run stability)**														
isotopic abundance		7.5	92.5	100	5.8	100	91.7	2.1	100	100	51.8	12.8	100	100
calibration blank (background) CPS:														
bk	average	48	48		3094	97	204320	2645	180		32	29		